Electrons in Disordered Structures

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CONTENTS

§ 1. INTRODUCTION

THE purpose of this article is to review recent experimental and theoretical work on the behaviour of electrons in disordered lattices. The experimental work falls into three main groups, as follows:

(*a*) The electrical and optical behaviour of liquid and amorphous (or glassy) semiconductors. Under this heading we include measurements of the mobility of carriers injected into insulating materials (e.g. liquid argon).

(*b*) The electrical and optical properties of liquid metals. On this, much theoretical work has been done recently, following Ziman's (1961) paper, assuming a *small* amplitude for the electron wave scattered by each atom. Most of this work is based on the 'one-electron model' of non-interacting electrons, although as we shall suggest correlation (electron–electron interaction) may be important particularly at densities near that at which a transition to the non-conducting state may be expected.

(*c*) Electrical and optical properties of heavily-doped semiconductors, the impurity centres being sufficiently close together to interact. We include under this heading concentrated solutions of alkali metals in ammonia. These phenomena will be discussed under two headings:

(i) The behaviour of weakly-interacting centres, in materials in which there is some compensation (i.e. some p-type centres in an n-type conductor). Here the conductivity is usually treated as temperature-activated hopping from centre to centre (Miller and Abrahams 1960, Mott and Twose 1961), and tends to zero with temperature.

(ii) Conduction in materials so heavily doped that the electrons in the centres behave like a degenerate electron gas (i.e. a metal), with a value of the conductivity tending to a finite value at the absolute zero of temperature.

The main purpose of the article is to examine how the behaviour of non-crystalline materials changes as the interaction of the electrons with the ions becomes stronger, or in other words as we go from the 'nearly free electron' to the 'tight binding' case. At one extreme we have materials with a long mean free path like liquid sodium, at the other materials which do not conduct at all, like fuzed quartz. Of particular interest are materials which are intermediate, such as liquid tellurium, some of the intermetallic compounds and mercury at high temperatures. Most of this is discussed in terms of the model of non-interacting electrons; the article includes however a brief review of our present knowledge about the transition between the metallic and the insulating state, because nearly all the evidence that this transition occurs is obtained from disordered systems.

Many of the arguments of this paper depend on the existence of solutions of the Schrödinger equation for an electron in an aperiodic lattice which are 'localized'. Such solutions are eigenfunctions and have quantized energy values and the wave function decays exponentially with distance from a point in space which is characteristic of the particular solution. In one dimension all solutions are known to be of this type; in three dimensions the problem has proved intractable, but it seems probable that the position is as follows:

(*a*) In disordered structures, if there are no large or extended density fluctuations, there *may* be no localized states; all bounded solutions of the time-independent Schrödinger eqn. (10) will extend throughout the lattice.

(*b*) In general, however, the lowest allowed states will be localized; there will be a critical energy E_c above which they are not. In this case, an electron initially in a localized state can move by thermally-activated hopping to another localized state, if the wave functions of the two states overlap enough to allow tunnelling between them; at each hop energy is given up or received through interaction with phonons. An electron can also move by the same process as in crystalline semiconductors, namely by thermal excitation to energies above E_c.

(*c*) Localized states may exist also in ranges of energy where the density of states is low, which can replace the regions of forbidden energy which exist for the electrons in a non-metallic crystalline solid. Such states are important for the understanding of liquid insulators and semiconductors.

When an electron is moving with energy above E_c, it will have a mean free path just as it would in a crystalline semiconductor or metal. If the mean free path is long compared with the wavelength, we can calculate it as is done by Ziman (1961) or Edwards (1962). If not, the theory of motion in an imperfect lattice has not yet advanced enough to enable calculations to be made. We shall give some reasons, however, for believing that at the critical energy E_c the mean free path L is of the order of the electron wavelength (calculated as for free electrons) and that values of L less than this are not possible. Mobilities less than $eL/m_{\text{eff}}v$, i.e. $eL/\hbar k$, where $kL \sim 1$, are due to hopping; k is here the wave number.

Throughout this report the emphasis will be on materials where the conductivity is on the borderline between the two processes.

Since localized states are so important for the considerations of this review, and since they are most completely understood in the one-dimensional case, I shall start with a discussion of this problem.

§ 2. ELECTRONS IN A DISORDERED ONE-DIMENSIONAL LATTICE

2.1. *Introduction*

As far as I know, the suggestion that for an electron in a disordered one-dimensional lattice all characteristic solutions of the Schrödinger equation are localized was first made by Mott and Twose (1961); these authors gave a proof for a particular model (a disordered Kronig–Penney lattice). This was extended by Borland (1961, 1963) and Borland and Bird (1964) to the case of a random distribution of delta functions. We think it worth while to set out the Mott–Twose argument in some detail.

What do we mean by the statement that states are localized? We mean that, if the Schrödinger equation for an electron in the field of a disordered potential V is:

$$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}(E-V)\psi=0, \qquad (1)$$

then all bounded solutions in the range $-\infty<x<\infty$ have a maximum value for some value x_n and decay exponentially to zero as

$$\exp\{-\gamma\,|x-x_n|\}$$

as $|x_n-x|$ tends to infinity. Each solution ψ_n has a characteristic energy value E_n. For an infinite lattice the energies E_n will form a continuous range; for a chain of length l they will be spaced at intervals proportional to $1/l$.

It may of course happen that a localized state has two (or more) peaks of comparable height at a distance, say, X from each other. If so, we should expect two states, in one of which ψ would have the same sign in both peaks, in the other opposite signs; the energy separation between them would be of order $E\exp(-\gamma X)$. As X increases, the proportion of configurations in which this happens will decrease exponentially.

2.2. *Strong Scatterers*; *the Model of Mott and Twose*

The random Kronig–Penney potential $V(x)$ is shown in fig. 1 (*c*). First consider an electron incident on a *single* potential step as in fig. 1 (*a*). It is well known that the bounded solution, shown by the full line in the upper diagram, is of the form $\sin(kx+\eta)$ for $x<0$, and that η is determined by the condition that ψ should decay exponentially for $x>0$, which gives:

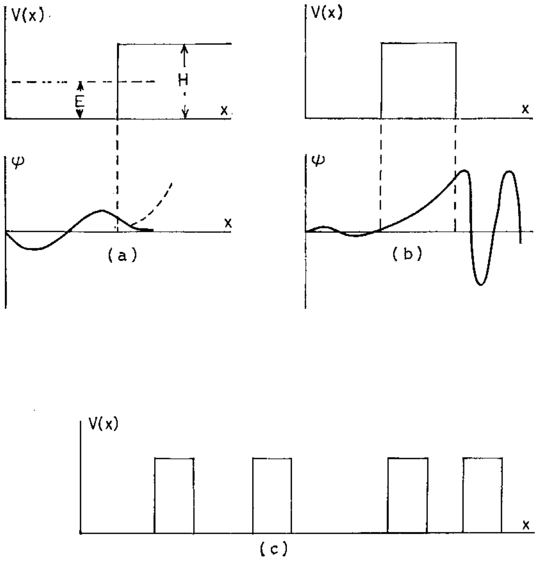
$$k\cot\eta=-\gamma,\quad \gamma=\surd\{2m(H-E)\}^{1/2}/\hbar.$$

For all other values of η the solution increases exponentially for $x>0$ as shown by the dotted line. Consider next a single Kronig–Penney step (fig. 1 *b*), and a wave function with the form $\sin(kx+\eta)$ for $x<0$. Then, except for a small range of η, ψ will *increase* on going through the step. Thus for a random array of steps (fig. 1 *c*), and starting to the left again with a solution $\psi=\sin(kx+\eta)$, we see that at most steps an exponential increase is expected, and that the amplitude of the solution will increase indefinitely as x increases.

At first sight this conclusion does not make sense; we could start on the right and by the same argument produce a solution which increases exponentially as x decreases. The clue to the apparent contradiction lies in considering the phases. It will be obvious from fig. 1 (*b*) that after passing through a large step in which ψ *increases*, the phase η' of the wave depends rather little on η. The behaviour of η' as a function of η is illustrated in fig. 2. The range AB of η is the range for which ψ decreases as x increases through the barrier.

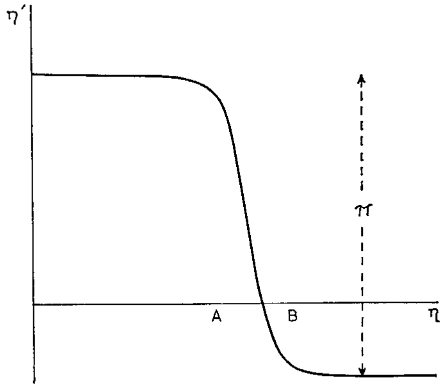
Consider now a large number of steps, and let η_0 be the phase in a given interval between steps, and η_n the phase in another interval some way to the right. Then if n is large, there will be a range AB of η_0 for which ψ decreases, and AB tends to zero with n; moreover, if η_0 does not lie in the interval AB, the phase η_n has a value approximately independent of η_0.

Fig. 1



Potentials and wave-functions ψ: (*a*) a single step, (*b*) a single barrier, (*c*) a disordered Kronig–Penney lattice.

Fig. 2

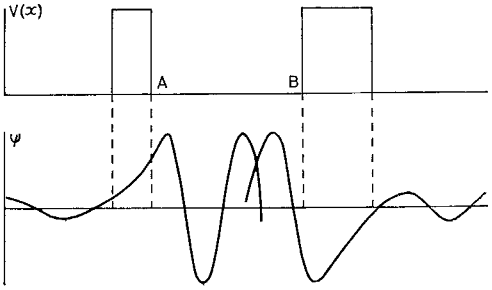


Phase η' at end of chain, a function of phase η at beginning.

We see therefore that there is one value of η_0 and one only for which, if we integrate (1) from left to right, ψ will decrease. For all other values it will eventually increase.

It follows that if we take a solution $\sin(kx+\eta_0)$ in a given interval between steps, we can choose η_0 so as to make ψ decrease for increasing x, *or* to decrease for increasing x, but not both. But if we vary k (i.e. the energy E), we can find solutions for a limited number of quantized values of E which decrease in both directions. This can best be seen by taking, as in fig. 3, solutions decreasing from left to right and from right to left and asking if they fit in the interval AB. The amplitudes are at our disposal so they will fit if the phases are the same. But for given energy the phases are fixed at A and B, so that (for big steps) it is obvious that as we change the energy we pass through a number of values for which the two do fit, with 0, 1, 2 . . . zeros of ψ in AB. These are the characteristic solutions of (1) localized round AB.

Fig. 3



Fitting the two halves of a localized wave-function ψ; $V(x)$ is the potential energy.

2.3. *Weak Scatterers*

The argument of the preceding paragraph applies only to very strong scatterers. The first proof that all states in any one-dimensional lattice are localized was given by Borland (1963) and Borland and Bird (1964), who treated a random chain of delta functions. Before considering this work, we give a more general argument which in § 3 we shall extend to three dimensions.

We shall first show that a wave impinging from outside on a random array of scatterers is totally reflected. Let the chain be as illustrated in fig. 4, the scatterers $P_1, P_2, \ldots$ being (say) delta functions. In the interval AB outside the chain take a solution of the Schrödinger equation which has the form:

$$\psi = \exp(ikx - i\omega t). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This represents particles going from left to right. Then, if L is the mean free path calculated by normal procedures, it follows that at distances a few multiples of L to the right of P_1 the particle is nearly as likely to be moving to the left as to the right; scattering will have made it forget its original direction of motion. Thus the solution there must be of the form:

$$[A \exp(ikx) + B \exp(-ikx)] \exp(-i\omega t), \quad . \quad . \quad . \quad . \quad (3)$$

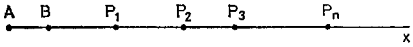
where A and B are slowly-varying functions of x and $(|A|^2 - |B|^2)/|A|^2$ is small compared with unity. But the current is conserved; so for all x:

$$|A|^2 - |B|^2 = 1.$$

Thus $|A|^2$ must increase exponentially with x as some multiple of $\exp(x/L)$.

If the sign of k in (3) is reversed, the solution represents a wave incident at P_n, nearly totally reflected and with a small amplitude transmitted.

Fig. 4



Points on a random lattice.

The solution (2) in the range AB has a real and imaginary part, $\sin kx$ and $\cos kx$. We have shown that *one* must increase, not necessarily both. In fact one can always choose one solution $\sin(kx+\eta)$ that will decrease. The demonstration that the only eigenstates for an infinite lattice are localized ones follows as in the model of Mott and Twose.

Borland's work considers in detail the behaviour of ψ at each delta function. The potential of a delta function at $x=0$ is defined by:

$$V(x) \quad = 0 \qquad x = 0,$$

$$\int V(x)\, dx = V_0 c.$$

The boundary conditions satisfied by ψ at $x=0$ are that ψ is continuous and $d \ln \psi/dx$ changes by $2mV_0c/\hbar^2$. Thus if we have a solution $\sin(kx+\eta)$ to the left of $x=0$, to the right $\psi = A \sin(kx+\eta')$, where

$$\sin\eta = A \sin\eta', \quad \cos\eta - A\cos\eta' = \theta,$$

where $\theta = 2mV_0c/\hbar k$.

Hence

$$A^2 = 1 + 2\theta\cos\eta + \theta^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$\tan\eta' = \sin\eta/(\cos\eta - \theta). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We can obtain the amount of scattering by each delta function by setting:

$$\psi = \exp(ikx) + A\exp(-ikx) \quad (x<0)$$

$$= B\exp(ikx) \qquad (x>0)$$

and applying the above boundary conditions. We find easily:

$$A = -i\theta/(2+i\theta).$$

Thus the scattered intensity is θ^2, to the first order in θ.

If the delta functions are distributed at random at a mean distance a from each other, the normal Boltzmann approach to a calculation of the mean free path L would give:

$$L = a/\theta^2. \qquad (6)$$

If, on the other hand, the distance between delta functions is distributed about the distance a with a mean square deviation $\Delta a (\Delta a \ll a)$, then we expect:

$$L = a/(k\Delta a)^2\theta^2, \qquad (7)$$

provided that ka does not lie near the values $n\pi$ for which Bragg reflection takes place.

We now look again at formulae (4), (5). We see that the value of A^2 averaged over all η is $1+\theta^2$. Thus, if the scattering centres are distributed at random, we expect (for small θ) that $|\psi|$ will increase on the average by the factor $1+\frac{1}{2}\theta^2$ on passing each scatterer. Thus, the envelope of $|\psi|^2$ will increase as $\exp(x/L)$, where L is defined by (6).

A similar proof can be given for the case (7). Thus the quantity that one would normally calculate as the mean free path appears as the length determining the rate at which ψ falls off or increases.

Turning now to the phase given by (5), it is obvious that after passing many steps the phase η_n behaves as illustrated in fig. 2. For any value of η_0 Borland shows that the successive application of this formula leads ultimately to a value η_n which is independent of η_0, unless one chooses the unique initial value η_c of η_0 for which ψ decreases. Localized states are set up by the same argument as before.

Borland's analysis has been discussed in detail in a review article by Halperin (1966) and also by Hori (1967).

In this section we have considered the bounded eigensolutions in an infinite chain. We can of course impose the cyclic boundary condition for a chain of length l that $\psi(x+l)=\psi(x)$ and $\psi'(x+l)=\psi'(x)$. For a long chain the effect on the form and energy of the eigenfunctions will be extremely small. Intuitively this must be so because very small changes in the energy and in the phase of ψ in the interval AB of fig. 3 will produce very large changes in these quantities at distant points where the boundary conditions must be applied.

Finally we emphasize that conductivity in a one-dimensional chain can only occur by hopping. If an electron is to jump from one state to another for which the orbitals overlap, energy must be exchanged with some heat source such as phonons. If kL is large the energy will be small, but still finite. This point is discussed further for the three-dimensional lattice in § 4.

2.4. *Density of States*

This is one of the earliest problems in this field to have been treated theoretically; it is particularly suitable for machine calculations (James and Ginzbarg 1953, Landauer and Helland 1954, Lax and Phillips 1958).

An analytical treatment is given by Frisch and Lloyd (1960). These papers use the following fact. For any real solution of the Schrödinger eqn. (1) defined in the range $0 < x < l$ with cyclic boundary conditions, we denote by ν the number of zeros in the range l and by ψ for the corresponding wave function. If we write:

$$K = 2\pi\nu/l,$$

then the density of states $n(E)$ is given by:

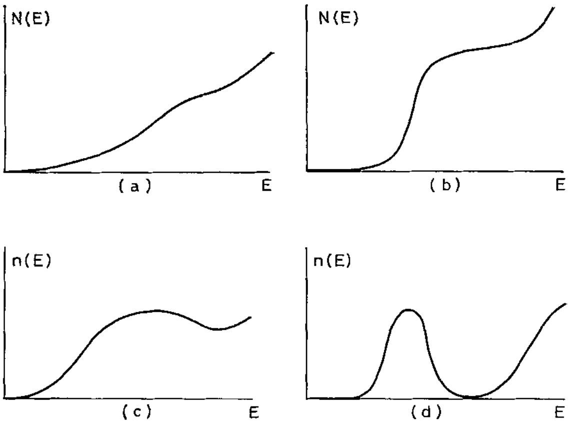
$$n(E) = l/2\pi(dE/dK)$$

and the integrated density:

$$N(E) = \int^{E} n(E)\, dE = lK/2\pi = \nu.$$

This conclusion is valid whether the solution is localized or not, and some of the calculations quoted were made before the localized nature of the wave functions was realized.

Fig. 5



Integrated density of states $N(E)$ (*a*) and (*b*) and differential density $n(E) = N'(E)$ (*c*) and (*d*) as calculated for one dimension by Frisch and Lloyd. (*a*) and (*c*) are for a high density of weak scatterers, (*b*) and (*c*) for a low density of strong scatterers (tight binding case).

Both Lax and Phillips and Frisch and Lloyd make calculations for a *random* distribution of attractive delta functions. At least one bound state will always exist in the field of an isolated delta function, of which these authors define the strength by the binding energy of the lowest state, which they write $-\hbar^2 K_0{}^2/2m$. The energy of an electron is then denoted by:

$$\hbar^2 k^2/2m, -\hbar^2 \kappa^2/2m,$$

for positive or negative values. The density of states thus depends on the dimensionless parameter nK_0, where n is the number of delta functions per unit length. Figures 5 (*a*) and 5 (*b*) show the plot of the integrated density N against k, κ (and thus $\sqrt{E}$ or $\sqrt{(-E)}$) for $nK_0 = 1$, $nK_0 = 0{\cdot}1$. Figures 5 (*c*) and 5 (*d*) show the differential density $n(E)$. The occurrence of a peak in the density of states when the atoms (delta functions) are well separated is marked. This corresponds to the tight binding case for periodic lattices. Landauer and Helland (1954) and Mackinson and Roberts (1962) were the first to discuss whether forbidden energy gaps persist in a disordered one-dimensional lattice. For a random distribution of centres they will not; the minimum of fig. 5 (*d*) will not drop to zero. But if the deviation from periodicity is small *and limited*, a gap may occur. In order to understand this, we examine the form of the solutions of the Schrödinger equation for values of E within the gap for a periodic structure with atoms distant a apart. These are of the form:

$$\psi = \sin(k_0 x + \eta) \exp(\pm \gamma x), \qquad \ldots \ldots \quad (8)$$

where $k_0 = \pi/a$, η varies by $\frac{1}{2}\pi$ within the gap and γ varies from zero at the extremities to a maximum value in the middle. The quantity γ can easily be calculated to the first order in the pseudopotential (Sommerfeld and Bethe 1933, p. 491, eqn. (29.18)). The result is:

$$\hbar^2 \gamma^2 / 2m = \{V^2 - (E - E_0)^2\} / \{2(E + E_0)\}.$$

Here E_0 is the energy of the middle of the gap and $2V$ is the width of the gap. Thus approximately:

$$\gamma = \tfrac{1}{2} k_0 \{V^2 - (E - E_0)^2\}^{1/2} / E_0$$

and

$$\gamma_{\max} \sim \tfrac{1}{2} k_0 V / E_0.$$

We see that γ is of the first order in V, not the second order as is $1/L$, where L is the mean free path. The quantity γ has recently been discussed in some detail in connection with the theory of surface states (Heine 1965) and for insulators can be measured experimentally by tunnelling (Lewicki and Mead 1966).

Suppose now that we have a disordered lattice in which the mean distance between the atoms is a and the width of the nth interval is $a + \Delta a_n$; we denote by $\overline{\Delta a}$ the root mean square value of Δa. Mackinson and Roberts (1962) pointed out that, if large values of a are allowed, then even if Δa is small the energy gap will disappear. States in the gap for which ψ falls off rapidly as $\exp(\pm \gamma x)$ (rather than slowly as $\exp(\pm x/L)$) will be located in regions where large values of Δa occur. If however there is a limit to the values that Δa may have, the gap may persist[†]. Schematic E, K curves

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[†] Hiroike (1965) concludes that gaps can exist for a Gaussian liquid if Δa is small enough. I do not think that this is correct and the conclusion depends on the method of averaging.

for these two cases are shown in fig. 6 (*a*) and 6 (*b*). Curves of this type were first computed by Landauer and Helland (1954). Taylor (1966) has given conditions for the persistance of the energy gap in three dimensions.

We may contrast the curves of the type shown in fig. 6 (*c*), which are published in Edwards' paper on one-dimensional lattices (Edwards 1961); here E is plotted against the *expectation value* of k, given say by $\sqrt{\overline{k^2}}$ where

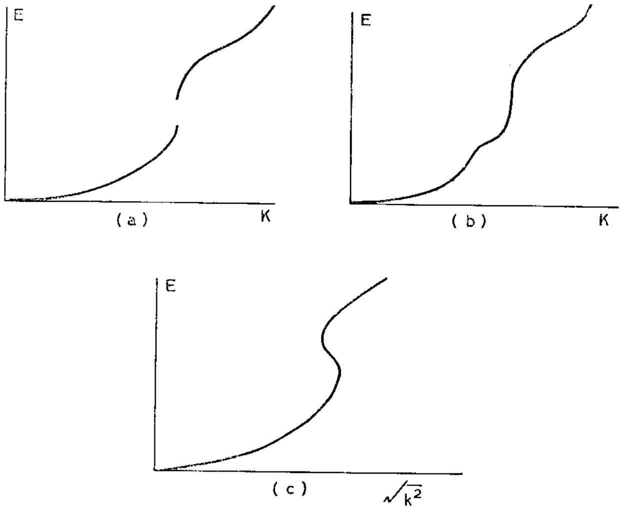
$$\overline{k^2} = \left\langle \int \psi^*(\partial^2/\partial x^2)\psi\, dx \right\rangle,$$

the $\langle\ \rangle$ denoting averaging over all configurations of the lattice. The reason for the behaviour shown is that in the region of the energy gap

$$\overline{k^2} \sim K_0{}^2 + \gamma^2;$$

since γ increases and then decreases as the energy increases, and K_0 is unchanged, $\overline{k^2}$ varies in the way illustrated.

Fig. 6



Curves plotting E against K (density of zeros in wave-function) (*a*) when the energy gap remains, (*b*) when it disappears. (*c*) shows the behaviour of E plotted against the expectation value of the momentum.

§ 3. Density of States in Three Dimensions

3.1. *Introduction*

The purpose of this section is to discuss the nature of the solutions of the three-dimensional Schrödinger equation:

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0, \qquad \ldots \ldots \quad (10)$$

and obtain the corresponding density of states. No complete solution of this problem has been obtained and quantitative work is limited to the use of perturbation methods (§ 3.2), discussion of the low energy tail and Anderson's (1958) tight binding model which will be discussed in this section. We therefore put forward a number of conjectures in support of which arguments will be given. These are:

(*a*) Within a given range of energies states are either localized or non-localized. This is a *qualitative* difference; if states are localized an electron placed in a given region will not diffuse away; the Kubo–Greenwood formula for the conductivity (§ 4.6) vanishes.

(*b*) There will thus exist critical energies E_c dividing ranges in which states are localized from those which are not (cf. fig. 7).

(*c*) For localized states ψ falls off as $\sin kr \exp(-\gamma r)$ and γ tends to zero as $E \to E_c$.

(*d*) For non-localized states, the mean free path L tends roughly to the electron wavelength λ as $E \to E_c$. Values of L smaller than λ (or $\lambda/2\pi$) cannot occur[†].

The only quantitative work on the condition for localized states is that of Anderson (1958). Anderson considers essentially the tight binding model, in which a single band of energy levels is formed from s-like atomic orbitals with bandwidth $2JZ$, where Z is the coordination number and J an overlap energy integral. Instead of considering a random variation of J due to an amorphous structure, Anderson imposes on each site a potential energy V, V having a random spread of values $\langle V \rangle$. He finds that if $\langle V \rangle / J$ is large enough, all eigenstates are localized; for smaller values some are not. His results are expressed in terms of the connectivity of the lattice, but it appears that states become localized when $\langle V \rangle$ is greater than about six times the band width. With this model there is no boundary E_c between localized and non-localized states.

The calculation can be applied to impurity-band conduction, of which a review is given in § 7.10 and for which the assumption of localized states and conduction by hopping has been made for a decade at least. Consider for instance n-type germanium, with a concentration of donors sufficient for appreciable overlap between their orbitals. If there are no acceptors present, one either has metallic conduction, or at lower concentrations, due to the Coulomb repulsion e^2/r_{12}, a non-conducting state; electrons can move only by excitation into the conduction band. But if some acceptors are present, some of the donors are unoccupied and e^2/r_{12} will no longer prevent electrons moving directly from one centre to another. At the same time, the charged acceptors produce a random field and thus a

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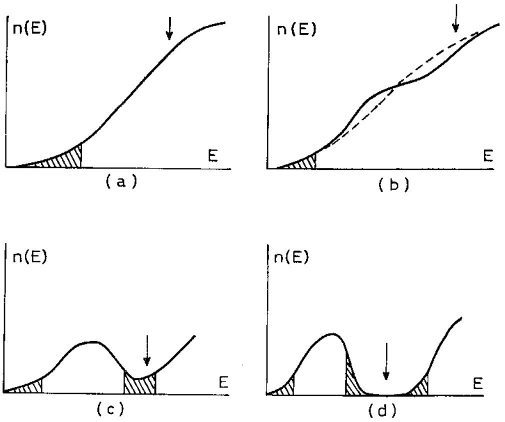
[†] Ioffe and Regel (1960) class the mobilities of semiconductors into those for which $\mu > 100$ cm^2 v^{-1} sec^{-1}; for these L is greater than the wavelength $h/\sqrt{(2mkT/3)}$; those for which $\mu < 5$ cm^2 v^{-1} sec^{-1} for which the mobility can only be explained if $L < a$, which they consider impossible; and intermediate values.

random potential of order $e^2/\kappa R$ at the donors; R is the distance between them. Whether the states are localized, or whether a band exists with a finite mean free path, will depend on Anderson's criterion. In the usual case, treated by Miller and Abrahams (1960), the states are localized (cf. § 7.10).

We turn now to the conduction band of a liquid metal or insulator. There is ample evidence that at the Fermi surface of liquid metals or disordered alloys the states are *not* localized; the conductivities of disordered alloys or amorphous metal films do not tend to zero with the temperature (§ 6.5). Moreover electrons excited into the conduction band of liquid argon have quite long mean free paths and the mobility is not trap-limited (§ 6.2). On the other hand, various authors have suggested that localized states may exist in a 'tail' below the 'conduction band' in amorphous materials (Fröhlich 1947, Gubanov 1963, Banyai 1964). We think that this is so, though in materials like liquid argon where the tail is due to density fluctuations it may be of little importance, while in glasses and amorphous polar materials it may be more marked[†].

Fig. 7



Suggested density of states for a three-dimensional lattice, with increasingly strong interaction with the lattice. The arrow shows the divalent Fermi energy. (*a*) is for nearly free electrons, showing a low energy tail, (*b*) is for weak interaction, (*c*) is for strong interaction, as for liquid tellurium, (*d*) is for a liquid semiconductor. The regions in which states may be localized are shown shaded.

Tails to the $N(E)$ curve have recently been considered by Lifshitz (1964), Bonch-Bruevich (1964) and Halperin and Lax (1966). What is meant is shown in fig. 7 (*a*). The tail in these treatments is due to density

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[†] In polar materials polarization round the trap will always increase the depth of a localized state (cf. § 4.3).

fluctuations, and it is assumed that compression lowers the bottom of the conduction band. In a liquid (or for that matter a solid) volumes in which the substance is compressed will contain potential wells. With a Boltzmann distribution of energies of such volume fluctuations there will be no limit to the depth of these wells. The energies of an electron in them will thus form a tail to the $N(E)$ curve of infinite extent, as in fig. 7 (*a*). Moreover, Anderson's (1958) theorem is applicable to these states; for the lower ones the spread of depths $\langle V \rangle$ will be large compared with the overlap integral J and therefore the states are localized. There will therefore be a boundary E_c as shown in fig. 7 (*a*) between energies where the states are and are not localized.

In § 4 we shall show that near this boundary the mean free path L and electron wavelength are comparable. This becomes plausible if, as in § 2.3 for the case of one dimension, we relate the existence or otherwise of localized states to the behaviour of a beam of electrons impinging on the crystal from outside. In the region of non-localized states, we should treat the passage through the crystal by a diffusion equation. If a beam of particles (N per unit volume, velocity v) falls on a slab of disordered material of thickness X, then one can achieve a steady state with a concentration $N(1-px)$ at a distance x from the surface. The rate of flow is DNp, where D is the diffusion coefficient, and the number emerging is $vN(1-pX)$. Equating these we determine p and find for the number coming out $vN/(1+X/L)$, where we have written $D=vL$, L being the mean free path. Intuitively we should expect this treatment to break down if $L \sim \lambda$. Also we should expect an exponential decay to occur below the conduction band in the tail of fig. 7 (*a*). We postulate that our energy E_c, separating localized from non-localized states, is also the energy where an exponential drop in the density of particles replaces a linear drop. A more detailed treatment of these considerations is given by Mott and Allgaier (1967).

Finally we have to ask in what way the density of states deviates from the free electron form on account of the non-periodic field apart from the 'tail'. First we must emphasize that, unlike the crystalline case, the *same* field is responsible for deviations and for the mean free path. Large deviations will always be associated with short mean free path.

We expect increasing interaction with the ions to produce $n(E)$ curves as in figs. 7 (*b*), 7 (*c*) and 7 (*d*). They are similar to what happens in the crystal with increasingly strong interaction, or in other words as the distance between the atoms increases. Curves like fig. 7 (*b*) can be obtained by perturbation theory as in the next section. The transition to the tight binding case has not yet been worked out for mixed s and p bands, which is what is required here. Nevertheless the general behaviour is likely to be as illustrated.

The interesting problem then arises as to under what conditions the states in the minimum will be localized. Naturally the situation may be different for liquid divalent metals, ionic crystals and so on. But in general, as we shall see, a perturbation strong enough to lower $N(E)$ by

50% will produce a mean free path of the order of the interatomic distance. We do not believe that mean free paths shorter than this can occur. Thus it seems very likely that localized states occur when the factor g, defined by $g = N(E)/N(E)_{\text{free}}$, falls below *about* 0·5. We shall see in § 6.7 that this conjecture describes well the behaviour of liquid semiconductors.

3.2. *Calculations of the Density of States using Perturbation Theory*

In this section we review the methods that have been used to determine the density of states by treating the non-periodic potential energy V as a small perturbation.

In the crystalline solid, second-order perturbation theory gives for the energy of a state with wave function of the type $\exp(i\mathbf{kr})\,u(\mathbf{r})$:

$$E = \frac{\hbar^2 k^2}{2m} + \langle \mathbf{k} \,|\, V \,|\, \mathbf{k} \rangle + \sum_{k'} \frac{|\langle \mathbf{k}' \,|\, V \,|\, \mathbf{k} \rangle|^2}{E_k - E_{k'}}, \qquad . \quad . \quad . \quad (11)$$

where the summation is over all points in k space for which the matrix element does not vanish. Since V is periodic with the period of the lattice, the vectors $\mathbf{k}'$ are of the type:

$$\mathbf{k}' = \mathbf{k} + \mathbf{n},$$

where $\mathbf{n}$ are the points of the reciprocal lattice. It should be noted that this formula is *not* a good approximation for points such that $|\mathbf{k}| \simeq |\mathbf{k}_n'|$—i.e. near energy gaps.

For the liquid or amorphous material (11) may be replaced by:

$$E = \hbar^2 k^2/2m + \langle \mathbf{k} \,|\, v \,|\, \mathbf{k} \rangle + \frac{\Omega}{8\pi^3} \int \frac{|\langle \mathbf{k}' \,|\, v \,|\, \mathbf{k} \rangle|^2 a(|\mathbf{k} - \mathbf{k}'|)\, d^3k'}{E_k - E_{k'}}, \qquad (12)$$

where $\langle \mathbf{k}' \,|\, v \,|\, \mathbf{k} \rangle$ is now the matrix element:

$$\Omega^{-1} \int v(r) \exp\{i(\mathbf{k} - \mathbf{k}')\mathbf{r}\}\, d^3x$$

of the scattering potential $v(r)$ of a *single* atom, the integral being over the atomic polyhedron of volume Ω, and $a(q)$ is the Fourier transform of the pair distribution function.

If $v(r)$ is a simple function of r, $\langle \mathbf{k}' \,|\, v \,|\, \mathbf{k} \rangle$ is a function of q only and may be written $v(q)$, where $q = |\mathbf{k} - \mathbf{k}'|$. Animalu and Heine (1965) and other authors make use of a 'non-localized' pseudopotential, that is one that operates differently on the s and p components of the wave-function; $v(q)$ will then be a function of E. In either case we may write (12) in the form:

$$E = \frac{\hbar^2 k^2}{2m} + v(0) + \frac{\Omega}{8\pi^3} \int \frac{|v(q)|^2 a(q)\, d^3q}{E_k - E_{k+q}}. \qquad . \quad . \quad . \quad (13)$$

The density of states for a liquid or amorphous material can then be evaluated from (13) using the formula (cf. Faber 1967):

$$n(E) = 4\pi k^2/8\pi^3\,(dE/dk). \qquad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

We note that corrections to the free-electron value arising from $v(0)$ will be the same in the liquid as in the solid (at constant volume); Animalu and

Heine give a table of calculated values of $v(0)$; for mercury for example the effective mass comes out to 0·69.

Most authors (e.g. Edwards 1962) consider only the second-order term and calculations of its magnitude have been made with various potentials by Watabe and Tanaka (1964), Lackmann-Cyrot (1964) and Schneider and Stoll (1967). Similar calculations for disordered alloys have been made by Jones (1966). We note that in the crystal, although $v(q)$ at reciprocal lattice points is seldom much greater than 1·5 ev (i.e. a band gap of 3 ev), it can produce rather large changes of $n(E)$ near the divalent Fermi surface; for instance in beryllium $n(E)/n(E)_{\text{free}}$ is 0·45 (for references to experimental and theoretical work see Mott 1966). It is not clear that this is true for the liquid, at any rate to the second order of approximation. The third term in (13), on integration over all directions of q, becomes:

$$\Delta E = \frac{m\Omega}{4\pi^2\hbar^2 k}\int |v(q)|^2 a(q) \ln\left|\frac{2k+q}{2k-q}\right| q\,dq.$$

To obtain an estimate of its magnitude, we write $|v(q)|^2 a(q) = F(q)$ and assume it to be a sharply peaked function of the form $A \exp\{-(q-q_1)^2/\sigma^2\}$. Then we find:

$$\frac{d(\Delta E)}{dk} \simeq -\frac{2m\Omega}{4\pi^2\hbar^2 k}\int \frac{F(q)\,q\,dq}{q-2k}$$

and dividing by $\hbar^2 k/m$ to find the correction to the free-electron form, supposing q_1 is quite near $2k_{\text{F}}$, we find approximately:

$$\frac{d\,\Delta E}{dk}\Big/\frac{\hbar^2 k}{2m} = \frac{3\sqrt{\pi}}{2}\frac{A}{E_{\text{F}}^2} f\left(\frac{2k-q_1}{\sigma}\right),$$

where†

$$f(x) = \frac{1}{2\sqrt{\pi}}\int_{-\infty}^{\infty}\frac{\exp(-t^2)\,dt}{t-x} = \exp(-x^2)\int_0^x \exp(t^2)\,dt.$$

The form of $n(E)$ with this correction is illustrated in fig. 7 (*b*); since q_1 lies below the divalent Fermi surface, $n(E)$ should be less than the free-electron value for a divalent metal. As regards the magnitude of the deviation, A will be equal to $|v(q_1)|^2 a(q_1)$, or about $2\cdot5\,|v(q_1)|^2$; f has a maximum value of about 0·5 when $(2k-q_1)/\sigma \sim 0\cdot8$, so a deviation of 50% (as for crystalline beryllium) would imply that $|v(q_1)/E_{\text{F}}|^2 \simeq 0\cdot15$.

Within second-order perturbation theory this procedure is not exact because—as already emphasized—one cannot treat the effect of $v(q)$ on the band form separately from the effect of v on the mean free path. Edwards (1958, 1961, 1962) was the first to treat the two together in a satisfactory way. Edwards derived the density of states $n(E)$, averaged over all configurations of the liquid, from the formula:

$$n(E) = \int \rho(E,k)\,d^3k, \qquad \ldots\ldots\ldots \quad (15)$$

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† See W. B. Thompson, *An Introduction to Plasma Physics*, p. 184.

where $\rho(k, E)$ is the 'mean square' probability of an electron having energy E and momentum k (Edwards 1961). Using a Green's function technique, factorizing the many particle correlation functions into products of pair correlation functions and neglecting odd terms in the expansion, Edwards (1962) sums the perturbation expansion and obtains:

$$\rho(E, k) = \Gamma/[\{E - \hbar^2k^2/2m + A(E, k)\}^2 + \Gamma^2]. \quad . \quad . \quad . \quad (16)$$

Here (Edwards 1962, p. 53) the quantity A is given by:

$$A(E, k) = \frac{1}{8\pi^3\Omega}\int \frac{|v(j)|^2 a(j)\, d^3j}{E - (\hbar^2/2m)(k-j)^2}, \quad . \quad . \quad . \quad . \quad (17)$$

and (Edwards 1962, p. 522)

$$\Gamma(E, k) = \int |v(j)|^2 a(j)\, \delta\{E - (\hbar^2/2m)(k-j)^2\}\, d^3j. \quad . \quad . \quad (18)$$

The term Γ will be discussed further in the chapter on the conductivity; it is a measure of the scattering by the centres in the Born approximation, and is just the expression used by Ziman (cf. § 4.2) in his theory of liquid metals.

If Γ is reasonably small, the contribution to (16) is large near the zero of the term in { }, and the main contribution to (16) comes from here. Since A is itself small, we may put $E = \hbar^2k^2/2m$ in the denominator of (16), so that ρ may be written:

$$\rho(E, k) = \Gamma/[\{E - E_1(k)\}^2 + \Gamma^2], \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where $E_1(k)$ is just the quantity (13). It is thus easily seen that (15) gives formula (14) for the density of states.

Calculation of the density of states using these formula, without the assumption that Γ is small, have recently been made for certain metals by Ballentine (1966).

3.3. *Does the Density of States Change on Melting?*

There is some evidence that for a number of metals the change in $n(E)$ at the Fermi surface is small on melting; this comes from the constancy of the Knight shift on melting of a number of metals shown in table 1 (Knight *et al.* 1959). The Knight shift should depend on the product of $n(E_F)$ and the penetration factor ξ; the latter is unlikely to change much; for the alkalis calculations by Lackmann-Cyrot (1964) confirm this. Ziman (1967) has suggested that this is because $N(E_F)$ is very near to the free-electron value for both solid and liquid, but we doubt if this can be the complete explanation. As we have shown in the last section, the use of perturbation theory does not suggest that there should be no change.

For one metal, aluminium, for which the band structure as shown by the L_{III} x-ray emission differs considerably from the free-electron form, there is little change in the emission spectrum on melting (Catterall and Trotter 1963). We may add that any large change in the density of states would be difficult to reconcile with the small latent heats of fusion.

Another piece of evidence for a small change is the work of Enderby *et al.* (1964) on the E.S.R. spin susceptibility of lithium, a metal for which there is thought to be a considerable deviation from the free-electron value of $n(E_F)$. These authors find that the change on melting is $1{\cdot}04 \pm 0{\cdot}05$.

Table 1. Change of Knight shift $\Delta H/H$ on melting (Knight *et al.* 1959)

	^{7}Li	^{23}Na	^{87}Rb	^{133}Cs	^{199}Hg	^{27}Al	^{119}Sn
Solid	0·0261	0·116	0·662	1·46	2·45	1·69	0·73
Liquid	0·0261	0·114	0·654	1·49	2·45	1·64	0·75

§ 4. CONDUCTIVITY; THEORY

4.1. *Metals, Semiconductors and Insulators*

The model illustrated in fig. 7 extends to non-periodic structures the explanation in terms of non-interacting electrons of the difference between insulators, semiconductors and metals first given for crystalline structures by Wilson (1931). If the Fermi energy lies in the non-shaded region the material is a metal and the resistivity tends to a finite value as $T \to 0$. Ordinary transport theory is applicable as long as the mean free path L is large compared with the electron wavelength λ. If the Fermi energy for low temperatures lies in the shaded region, the material is a semiconductor or insulator. Conductivity is then possible by two processes:

(*a*) Excitation into the unshaded region; the process by which a current is carried is then the same as in a crystalline semiconductor.

(*b*) Hopping from one localized state to another. This always involves an activation energy, because each localized state has its own quantized energy value. It may also involve tunnelling. One expects smaller activation energies than for process (*a*). Thus process (*b*), which is entirely analogous to impurity-band conduction by hopping (§ 7.10), should be predominant at low temperatures. Moreover, for reasons to be given in § 4.3, the activation energy should drop with decreasing T.

One important consequence of this model has been emphasized particularly by Gubanov (1963); it predicts that amorphous semiconductors should be less sensitive to doping than crystalline ones. Donor impurities for instance must be present in sufficient concentration to shift the Fermi level appreciably, if they are to affect the 'intrinsic' conductivity, i.e. the number of electrons excited into the non-localized part of the energy spectrum. Of course, if they increase the number of available localized states near the Fermi energy, they may greatly increase the hopping probability (cf. § 6.4).

4.2. *Weak Scattering*

Ziman (1961) was the first to point out that the conductivity of most metals can be accounted for by the assumption that the scattering of an electron wave by each atom is small, and that it can therefore be calculated from the atomic pseudopotential by using the Born approximation for the scattering and the experimentally determined pair distribution functions for the relative positions of the atoms. The case of total disorder will be discussed first. Here the conductivity should be given by:

$$\sigma = Ne^2\tau/m, \qquad (20)$$

where

$$1/\tau = N_i v \int_0^\pi I(\theta)\,(1-\cos\theta)\,2\pi\sin\theta\,d\theta.$$

N_i is the number of scattering centres per unit volume, N the number of electrons and (for a metal) v the velocity of an electron at the Fermi surface. This formula has been used for many years to calculate the resistivity of dilute alloys, $I(\theta)$ being then the scattering due to the difference between the solute and solvent atoms (Nordheim 1931, Mott and Jones 1936, p. 286). It has been used by Mott and Twose (1961) and others (cf. § 7.8) to calculate the resistivity of a heavily doped semiconductor due to the randomly distributed impurity centres.

For a liquid, however, the atoms are not randomly distributed, and one must introduce the pair distribution function. This was first done by Bhatia and Krishnan (1948) and the development of the idea and its comparison with experiment are due to Ziman. The idea is the following.

Taking any one atom, let $P(R)d^3R$ be the probability that another atom is present at distance R. The intensity scattered by two atoms at distance R from each other is:

$$I(\theta)\,|1+\exp\{i(\mathbf{k}-\mathbf{k}'\,.\,\mathbf{R})\}|^2.$$

Averaging over all R, we obtain the scattered intensity $I(\theta)a(q)$, where

$$a(q) = \int_0^\infty |1+\exp[i(q,\mathbf{R})]|^2 P(r)\,d^3R \qquad (21)$$

and

$$q = |\mathbf{k}-\mathbf{k}'| = 2k\sin\tfrac{1}{2}\theta.$$

An angular integration gives:

$$a(q) = 1 + \frac{N}{V}\int \{P(R)-1\}\frac{\sin qR}{qR}\,4\pi R^2\,dR.$$

$a(q)$ is just the quantity determined experimentally from the scattering of x-rays or neutrons by the liquid. It is known experimentally, and most attempts to calculate σ use experimental values; Ashcroft and Lekner (1966) have used theoretical values deduced from the Percus–Yevick theory of liquids.

The conductivity is then given by (20) with

$$1/\tau v = 1/L = N_i \int I(\theta)\,(1-\cos\theta)\,a(q)\,2\pi\sin\theta\,d\theta. \qquad (22)$$

Ziman and his collaborators then determine $I(\theta)$ from the calculated pseudopotential $v(r)$ of the ion in the liquid, or from an estimate of phase shifts or in some other way. If one uses the Born approximation, then

$$I(\theta)=\left|\frac{m\Omega}{2\pi\hbar^2}v(q)\right|^2,$$

where

$$v(q)=\Omega^{-1}\int v(r)\exp\left[i(\mathbf{qr})\right]d^3x, \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where the integration is over a cell of volume Ω.

It can easily be verified that Edwards' quantity Γ (§ 3.2) is equal to $\hbar/\tau$ of Ziman's theory.

The developments which have followed from Ziman's theory are as follows.

(*a*) Attempts to calculate the absolute values of the resistivity. Here results are very sensitive to the position of the zero in $v(q)$—i.e. the angle at which the scattering vanishes; absolute values are therefore perhaps of little significance. Ashcroft and Lekner (1966) give a table showing the very large variations in the calculated values that result from the choice among current calculated values of $v(q)$. They use experimental and theoretical values of $a(q)$ (Percus and Yevick 1958).

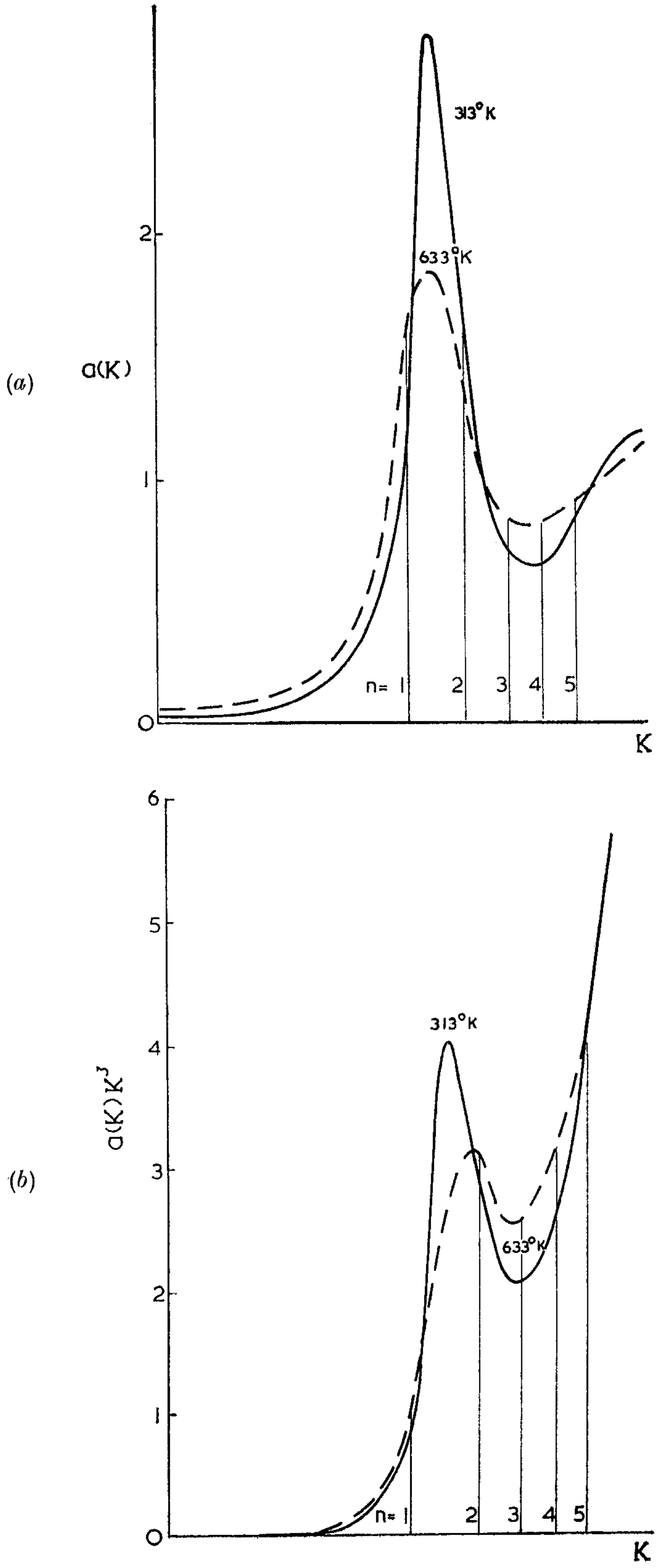
(*b*) Treatment of the temperature-dependence of the resistivity. The successful treatment of this is perhaps one of the greatest successes of the theory, particularly as it explains the difference between monovalent and divalent metals (Bradley *et al.* 1962). Figure 8, taken from this paper, shows a typical x-ray scattering function at two different temperatures, with $2k_{\mathrm{F}}$ shown for metals of different valency. The plot is against q (i.e. $4\pi\sin\frac{1}{2}\theta/\lambda$). For small q, $a(q)$ will increase with temperature and indeed for very low q it depends only on macroscopic fluctuations of density and is given by the Ornstein–Zernike formula:

$$a(q)=kT/\kappa\Omega, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where κ is the bulk modulus and Ω the atomic volume. At constant volume one expects $v(q)$ to be independent of temperature and so in general we expect $(d\rho/dT)_{\mathrm{V}}$ to be positive for monovalent metals and negative for divalent. For the experimental observations, see for instance Cusack (1963), Ziman (1967).

(*c*) Liquid alloys have been discussed by Faber and Ziman (1965). Here, if there are two components 1 and 2, one has two scattering pseudopotentials v_1 and v_2 and three different correlation functions a_{11}, a_{12} and a_{22}. Faber and Ziman's analysis is based on the assumption that all three coefficients a_{rs} are identical. The most interesting result is the difference in the behaviour of monovalent and polyvalent metals; for the former $a(q)$ cuts down the scattering below that for a random distribution; then, as for crystals, the resistivity shows a striking maximum for somewhere near

Fig. 8



Typical x-ray distribution function $a(K)$ for a liquid at two temperatures, wit $2k_F$ for n electrons per atom shown (Bradley *et al.*).

equal concentrations of the two constituents. For divalent and polyvalent metals, for which $a(q)$ is of order unity for values of q giving significant scattering, the resistivity appears much more nearly additive.

Only recently have attempts been made to obtain the quantities α_{11}, a_{22}, a_{12} separately. Thus Steeb and Entress (1966) deduce from x-ray measurements that in Mg–Sn each Mg atom tends to be surrounded by Sn and vice versa, while Enderby *et al.* (1966) have compared x-ray and neutron diffraction patterns in CuSn. If a_{12} is not equal to a_{11} (as for instance for liquid NaCl), we should write instead of $a(q)\{v(q)\}^2$ for a binary alloy:

$$c_1 a_{11} |v_1|^2 + c_2 a_{22} |v_2|^2 + 2(c_1 c_2)^{1/2} a_{12} |v_1 v_2|. \quad . \quad . \quad . \quad (25)$$

For simplicity let us take $c_1 = c_2 = \frac{1}{2}$, $a_{11} = a_{22} = a$ and write:

$$v_1 = v + \delta, \quad v_2 = v - \delta;$$

we find:

$$a|v|^2 + a_{12}\delta^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

In liquid compound semiconductors we should expect each atom to be surrounded mainly by atoms of the opposite kind. Thus a_{12} will have a peak at $q \sim r^{-1}$, where r is the interatomic distance. For liquid semiconductors and intermetallic compounds δ must be fairly large to produce a band gap in the solid; so the term $a_{12}\delta^2$ should have a very large effect on the resistivity, and should be responsible for a dip in the density of states. Since the peak in a_{12} widens rapidly with temperature, we expect a positive value of $d\sigma/dT$ even if states are not localized.

(*d*) It is clear that on the nearly free-electron model the Hall constant should have the free electron value. Some discrepancies are discussed in § 4.5.

For semiconductors, or electrons injected into an amorphous conduction band (e.g. liquid argon), formulae (22) and (23) reduce to that given by the familiar treatment with a deformation potential. We are only interested in small changes of q, so that $a(q) = kT/\kappa\Omega$ and $v(q) = v(0)$. Thus:

$$1/L = (kT/\kappa)\{2mv(0)/\hbar^2\}^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

We see that this reduces to the deformation band treatment as follows. A fluctuation of density $\Delta\rho/\rho$ will produce a change in the energy of the bottom of the conduction band $v(0)$ equal to $v(0)\Delta\rho/\rho$. The scattering cross section by such a fluctuation if the fluctuation extends over a radius r_0 is:

$$\left\{\frac{2m}{\hbar^2} v(0) \frac{\Delta\rho}{\rho} r_0^3\right\}^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

The energy of such a fluctuation is:

$$\tfrac{1}{2}\kappa(\Delta\rho/\rho)^2 r_0^3 \sim kT, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

so substituting for $\Delta\rho$ we obtain for the scattering cross section:

$$(kT/\kappa)\{2mv(0)/\hbar^2\}^2 r_0^3,$$

and since there are $1/r_0^3$ centres per unit volume, formula (27) for $1/L$ follows for all values of r_0.

It is interesting in this connection to see that our formula $kL \sim 1$ for the appearance of localized states is valid. The condition that a localized state will occur is:

$$(2m/\hbar^2)(\Delta\rho/\rho)\, v(0) \gtrsim 1/r^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Thus at any temperature the larger fluctuations form localized states, which give the tail of the conduction band. When the wavelength λ of the electron is comparable with the value of r given by (30), we expect localized states to occur. It is very easily verified using (29) that (30) leads to $\lambda \sim L$, if L is given by (27).

4.3. *Conductivity by Hopping*

In the evaluation of the conductivity due to hopping there are two separate problems to consider.

(*a*) The evaluation of the probability per unit time that the electron jumps from one localized state to another. This we shall write:

$$\nu p(R) \exp\{-(\Delta W + \tfrac{1}{2} W_{\rm p})/kT\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Here ν is a phonon frequency; $p(R)$ is a tunnel factor which must be introduced if the distance R between the states is large. If ψ falls off as $\exp(-\gamma r)$, $p(R) = \exp(-2\gamma R)$. For impurity levels having a mean energy W below a conduction band, $\gamma = \sqrt{(2mW)}/\hbar$. W is the difference in energy of the two levels and $W_{\rm p}$ is the energy of polarization round a localized state of order:

$$W_{\rm p} = \tfrac{1}{2}\frac{e^2}{r_0}\left(\frac{1}{\kappa_0} - \frac{1}{\kappa}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

where r_0 is the radius of the state and κ, κ_0 the dielectric constants.

(*b*) Recognizing that $p(R)$ and ΔW will both vary greatly from one jump to another, one has to average over all possible jumps to obtain the a.c. or d.c. conductivity. Results of such averaging show:

(i) That the a.c. conductivity is higher than the d.c. and increases with frequency (cf. papers by Pollak quoted in § 7.10).

(ii) The activation energy for conduction drops with decreasing temperature, since at low temperatures only hops with small ΔW can occur, even though R may be large and $p(R)$ small.

All the calculations on disordered structures known to the author have been for the case of impurity-band conduction; these are reviewed in § 7.10.

More attention in the literature has been given to the theory of the hopping motion of polarons, to which the phenomenon described here is closely allied. Moreover, as we have stated, the lattice round an electron in a localized state will be strongly polarized in ionic crystals, and distorted to some extent for non-polar crystals. Reviews of polaron theory have been given by Fröhlich (1954, 1963); a useful summary of the present position can be found in an article by Jortner *et al.* (1965). A very brief account is given here.

A coupling constant

$$\alpha = e^2\left(\frac{1}{\kappa_0} - \frac{1}{\kappa}\right)\sqrt{\frac{m}{2\omega\hbar^3}}$$

is introduced; here m is the effective mass in the undisturbed lattice and ω the frequency of optical phonons. If α is less than about 10, the motion of the ions can adjust itself to the motion of the electrons, and the sole effect is somewhat to increase the effective mass ($m_{\text{eff}}/m \simeq 1+\alpha/6$ if $\alpha \ll 1$) (Fröhlich 1963, Brown 1963, Langreth and Kadanoff 1964, Mahan 1966); values of α less than unity are estimated for PbS, GaAs and values of about 5 for the alkali halides.

If $\alpha > 10$, on the other hand, theory predicts what is known as the 'small polaron', an electron being effectively trapped by the potential well produced by the surrounding polarized medium, as envisaged by Landau (1933; see also Mott and Gurney 1940, p. 87). At low temperatures it moves without thermal activation, though with very high effective mass. As the temperature increases, the effective mass *increases* and the mean free path decreases. At a temperature of the order $\frac{1}{2}\Theta_{\text{Debye}}$ the mean free path becomes of the order of the interatomic distance, and for higher temperatures than this the motion is properly described as thermally activated hopping (Holstein 1959), the mobility being of the form:

$$\mu = (\nu e a^2/kT)\exp(-\Delta E/kT), \qquad (33)$$

where ΔE is about half the trapping energy W_{p}. On each hop phonons are emitted and absorbed. This factor $\frac{1}{2}$ occurs in any transfer from one polarized state to another, for instance in the $Fe^{3+} \rightarrow Fe^{2+}$ transfer in aqueous solutions. For a theoretical treatment see Mott and Watts-Tobin (1961). We may mention that trapping by distortion of the lattice is also possible in non-polar semiconductors; calculations for this case have been made by Glarum (1963, see also Toyozawa 1963) for narrow band organic semiconductors, and he finds a formula of type (33) where again ΔE is half the energy necessary for trapping†. Also in liquids trapping is possible, either by the same mechanism or by cavity formation or both (see § 7.3).

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† In a contribution to the theory of organic semiconductors, Friedman (1964) points out that, though the band width W may be less than kT, the 'polaron' trapping energy is less still and the mobility is not of small polaron type, behaving as T^{-n} with $3 < n < 1$. Implicitly by writing $(\hbar/\tau) < W$ as the condition for a band formulation, Friedman uses our formula $kL \gtrsim 1$ for localized states *not* to be formed. With this condition Friedman finds that for narrow bands

$$\mu \geqslant 0{\cdot}1\ (W/kT)\ \text{cm}^2/\text{v sec.}$$

Lower values than this must mean hopping.

There has recently been some uncertainty as to which observed forms of conduction are due to polaron hopping, particularly in the case of NiO doped with small quantities of lithium. Until recently it was believed that this was due to hopping by a small polaron but recent experiments by Springthorpe *et al.* (1965), and Austin *et al.* (1967) and Bosman and Crevecoeur (1966) suggest that this is not so; the evidence is based on the thermoelectric power and is reviewed below. On the other hand, Snowden and Saltsburg (1965) have given evidence that positive holes bound to Li^+ ions in NiO do form polarons and move round the ion by hopping (see also Appel 1966).

Perhaps one of the clearest examples of a hopping process of polaron type in a non-polar crystal is the recent work of Spear and his colleagues on the mobility of electrons and holes in orthorhombic sulphur produced by electron bombardment of the surface (Adams *et al.* 1964, Adams and Spear 1964, Gibbons and Spear 1966). Holes have a high mobility of the normal type. Electrons on the other hand have a low mobility

$$6 \times 10^{-4}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}\,\mathrm{v}^{-1} \text{ at } 21\,^\circ\mathrm{c}$$

with an activation energy of 0·167 ev. The consistency of the results indicated a hopping polaron motion, the polaron energy being estimated from current theories as 0·48 ev. Spear estimates an overlap integral between sulphur rings of *ca.* 0·05 ev, so the coupling constant α must be large (>15).

4.4. *Thermoelectric Power*

The following are useful formulae for the interpretation of the thermoelectric power. For semiconductors in which a non-degenerate gas of carriers are in a single band with density of state proportional to $\sqrt{E}$, one can write (Jonker and Houten 1961):

$$\alpha = (k/e)\{\ln(N_V/n) + r + 2\}. \qquad (38)$$

Here $N_V = (2\pi mkT/\hbar^2)^{3/2}$ and n is the number of carriers per unit volume. The constant r depends on the mechanism of scattering and should be zero if the scattering is by acoustic phonons. If the n carriers are excited from N levels at an energy E below the band,

$$n^2 = NN_V \exp(-E/kT),$$

and the dominant temperature-dependent term in α is $(k/e)(E/2kT)$, so the thermoelectric power plotted against $1/T$ should give, approximately, a straight line.

Heikes and Ure (1961) have considered a simple case of localized electrons, in which there are N sites, all with the same energy, and N_c are occupied; localization is due to small polaron formation. The thermopower is then†:

$$\alpha = (k/e)\,[\ln\{c(1-c)\} + \text{const.}]. \qquad (39)$$

---

† Howard and Lidiard (1957 a, b) discuss the similar problem of ionic conduction.

The constant depends on the mechanism of hopping and has not been evaluated. It will be seen that the logarithm can have positive or negative values, but e is always the (negative) charge on the electron. The formula is applied to glasses containing transition metal ions in § 7.11.

If electrons are excited into a narrow band in which small polarons are formed, then (38) is valid if for N_V we write the number of sites; for the hopping mechanism, however, we do not know r.

As far as we know, hopping between levels of differing energy, as in impurity-band conduction, has not been treated. However, here one has a distribution of energy levels and at low temperatures a Fermi limiting energy E_F and the formula used for metals should be valid, namely:

$$\alpha = \frac{\pi^2}{3}\frac{k^2T}{e}\left\{\frac{\partial \ln \sigma(E)}{\partial E}\right\}_{E=E_F}, \quad \ldots\ldots \quad (40)$$

σ will be of the form $\sigma_0(E)\exp[-W(E)/kT]$ and both terms should vary strongly with E; thus we expect a constant term and a term linear in T.

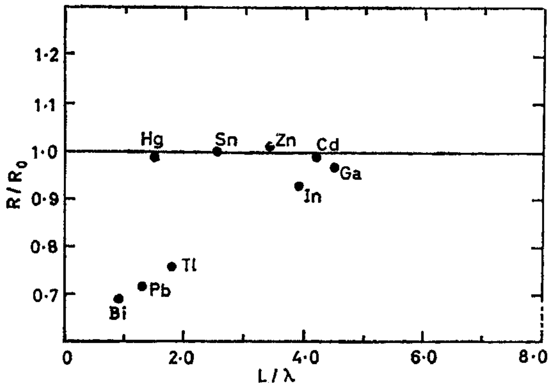
4.5. *Hall Coefficients*

For a crystalline metal the Hall coefficient R should have the free-electron value

$$R = 1/Nec$$

for any form of Fermi surface which does not give open orbits. For liquid metals the Hall coefficients are much closer to the free-electron values than for the solids (see reviews by Cusack 1963, Busch and Tièche 1963 and Ziman 1967). Figure 9 shows some measured values due to Greenfield (1964); they are plotted against L/λ, to show that discrepancies are more likely to occur for metals with short mean free path.

Fig. 9



Measured values R of the Hall coefficient as a function of L/λ, as a fraction of the value R_0 calculated on the free-electron model.

Of course if L/λ is not large it is impossible to define a Fermi surface with any precision; the free-electron values of R for metals for which

$L/\lambda \gg 1$ are often quoted as evidence that the Fermi surface is spherical. If L is large compared with any distance within which local order exists, any form of Fermi surface other than spherical seems difficult to envisage.

The only treatment of the Hall effect known to the author in which the Hall constant, for non-hopping, is calculated for $L \sim \lambda$ is that of Banyai and Aldea (1966), who start from Kubo's formulation (cf. the next section). They conclude that for a spherical Fermi surface R will depend on the departure of the density of states from the free-electron value. Taking a form of $n(E)$ appropriate to an impurity band, they conclude that R may even change sign if $n(E)$ decreases with E. If these results are correct, there should be little difficulty in accounting for the observed deviation from the free-electron formula. We give in § 6.7, in our discussion of tellurium, empirical evidence that the Hall coefficient can depend on the density of states.

For hopping conduction there have been extensive theoretical calculations mainly for hopping by the small polaron (Friedman and Holstein 1963, Firsov 1964, Schakenberg 1965) and also for localized states in impurity-band conduction (Holstein 1961). This work all shows that a quite large Hall effect is to be expected and that it will be very difficult to calculate its magnitude. The argument in its simplest terms is the following. Suppose we have n carriers per unit volume; then at any one time the magnetic field can only affect those that are in the process of hopping, and thus a fraction $\exp(-\Delta E/kT)$. These too will only be affected by the magnetic field if they have a choice of sites into which to hop with just the right energy; this will be determined by another exponential factor $\exp(-W/kT)$. They thus argue that the Hall coefficient will be of order:

$$1/R = nec \exp\{(W-\Delta E)/kT\}, \qquad (41)$$

where n is the density of current carriers. They also state that ΔE and W are of the same order and that W may be less than ΔE, so that R can be greater than $1/nec$. This formula does not take account of the tunnel factor $p(R)$. The two sites into which the electron must jump must have nearly the same value of p and the chance that this is so will certainly be of order $p(R)$. But the Hall voltage will be determined by the easiest jumps, while the d.c. conductivity by the most difficult. So I would expect (41) to give too large a value of $1/R$, and that R should be enhanced by some factor of the type $\exp(-2\beta R)$, with $\beta < \alpha$.

The application of these ideas to localized states due to disorder (impurity-band conduction) will be complicated by the random distribution of hopping frequencies and the answer should depend on the period of an a.c. field. These points have been discussed by Amitay and Pollak (1966) who have at the same time attempted to observe the Hall effect in doped and compensated silicon. They observed no effect, and concluded that Holstein's original calculation gave results very much too large.

On the other hand, Kyser and Thompson (1965) have observed a large Hall effect in solutions of sodium in ammonia for concentrations where conductivity is probably by hopping (§ 7.3), and this is perhaps one of the few cases where a Hall constant has been measured in the hopping region.

Measurements of the Hall effect of ions in solution have been made by Laforgue-Kantzer (1965); here too the theoretical position is not clear.

4.6. *Intermediate Case; Strong Interaction with Ions but States not Localized*

In this section I shall discuss the case intermediate between those treated previously; interaction with the ions is strong, so that there can be substantial deviations from the free-electron density of states, and the mean free path is short, but at the Fermi energy the states are not localized. The theory is thus applicable to liquids such as tellurium and liquid intermetallic compounds and also possibly to doped semiconductors under certain conditions.

Since the mean free path is necessarily short, no precise concept of a Fermi surface can be used since the uncertainty Δk in the wave-number k is large. On the other hand, there will be a clearly-defined Fermi limiting energy E_F. Under these conditions it is appropriate to calculate the conductivity σ from the Kubo–Greenwood formula (Kubo 1956, Greenwood 1958), according to which at $T=0$:

$$\sigma = \frac{2\pi e^2\hbar^3}{m^2} \sum_n \sum_{n'} |D_{nn'}|^2 \delta(E_F - E_n)\delta(E_F - E_{n'}), \tag{42}$$

where E_F is the Fermi energy and

$$D_{nn'} = \int \psi_n{}^* \frac{\partial}{\partial x} \psi_{n'}\, d^3x \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{43}$$

and the ψ_n are eigensolutions of the Schrödinger equation with appropriate boundary conditions and with energy E_n for an electron in a disordered lattice. The simplest way to prove this formula is to treat it as the limit as $\omega \to 0$ of the formula for the current produced by a light wave of frequency ω. This treatment is given in § 5.

We have first to ask whether, if the Fermi energy lies in the range of localized states, the Kubo formula predicts zero conductivity at zero temperature. Here we have to distinguish between

(*a*) The d.c. conductivity.

(*b*) The a.c. conductivity in the limit of weak fields.

Common sense and experience with impurity-band conduction suggest that the d.c. conductivity does tend to zero as $T \to 0$; the Kubo formula shows that this is so, since if ψ_n, $\psi_{n'}$ are localized states with energies very near the Fermi level, it will be a rare 'accident' that they are near enough in space to overlap and thus to give a finite value of $D_{nn'}$. Some treatments of the problem (e.g. Day 1966) have come to the conclusion that when one averages the current over all configurations of the lattice, these accidents will occur and lead to a finite current. This conclusion appears to be wrong (Halperin 1967); $\sigma(\omega)$, the conductivity at frequency ω, tends to zero like ω^2 as ω tends to zero. This is proved in § 5.

When the states are localized, then, there can only be a current at a finite temperature due to the interaction with phonons, a process not included in formula (42).

We turn then to the case of non-localized states which is the main subject of this section. The usual formula for the conductivity of a solid in the case of nearly free electrons is:

$$\sigma = ne^2\tau/m,$$

where τ is the time of relaxation; this can conveniently be expressed in the form (Ziman 1961):

$$\sigma = Se^2h/12\pi^3\hbar, \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

where S is the area of the Fermi surface and L the mean free path.

We have to show that in the case of weak interaction (44) follows from the Kubo formula. We shall also show that, if the interaction is strong enough appreciably to modify the density of states, formula (44) becomes:

$$\sigma = Se^2Lg^2/12\pi^3\hbar, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

where

$$g = n(E_F)/n(E_F)_{\text{free}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

This formula does not depend on perturbation theory, and should be valid as long as the states are not localized (Mott 1966), and as long as $g < 1$. If $g > 1$ (the tight binding case), (44) should be used.

In making this statement we must define the mean free path. Alternatively we can say:

(*a*) It is the distance L in which two wave functions ψ_n, $\psi_{n'}$ both behaving like exp (ikx) at a given point, remain coherent.

(*b*) It is the reciprocal of the uncertainty in k derived from Fourier analysis of ψ.

(*c*) Following Ziman (1966), we can envisage a complex wave number

$$k = k_0 + i\gamma;$$

L is then $1/\gamma$. This is correct as long as E is *not* in the energy range where states are localized; if it is, there is no mean free path and γ has a different meaning.

A discussion of the mean free path is given in the next section. We turn now to methods by which the Kubo–Greenwood formula can be shown to give formulae (44) and (45). There are two ways available. The first, due to Edwards, is as follows. Formula (42) may be written:

$$\left\langle \int\!\!\int \sum\sum \psi_n(\boldsymbol{x}_1)\nabla_1\psi_{n'}(x_1)\,d^3x_1\,\psi_{n'}(x_2)\nabla_2\psi_n(x_2)\,d^3x_2\,\delta(E-E_n)\delta(E-E_{n'})\right\rangle,$$

where the sign $\langle\ \rangle$ denotes averaging over all configurations of the atoms. This can be rearranged to give:

$$\iint \left\langle \sum_n \psi_n(x_1)\nabla_2\psi_n(x_2)\delta(E-E_n)\sum_{n'}\psi_{n'}(x_2)\nabla_1\psi_{n'}(x_1)\delta(E-E_{n'}) \right\rangle d^3x_1\,d^3x_2,$$

the averaging now being done before integration. This is now replaced by

$$\iint \left\langle \sum_n \psi_n(x_1)\nabla_2\psi_n(x_2)\delta(E-E_n) \right\rangle \times \left\langle \sum_n \psi_n(x_2)\nabla_1\psi_n(x_1)(E-E_n) \right\rangle d^3x_1\,d^3x_2.$$

The interference between these two terms is treated by Edwards (1958) for a random distribution of weak scatterers, and its neglect shown to be justified, apart from the factor $(1-\cos\theta)$. As Edwards states, the method can be extended to any homogeneous distribution, in the case of weak interactions. We therefore set:

$$\left\langle \sum_n \delta(E-E_n)\,\psi_n(x_1)\,\psi_n(x_2) \right\rangle = \int \sum_n P(\mathbf{R}_1,\mathbf{R}_2\ldots)\prod d^3R_n\,\psi(x_1\,;\mathbf{R}_1,\mathbf{R}_2\ldots) \times \psi^*(x_2\,;\mathbf{R}_1,\mathbf{R}_2\ldots)\delta(E-E_n),$$

where P is the probability distribution of the atoms. If the system is homogeneous, then for any vector $\mathbf{a}$:

$$P(\mathbf{R}_1+\mathbf{a},\ \mathbf{R}_2+\mathbf{a},\ldots)=P(\mathbf{R}_1,\mathbf{R}_2\ldots).$$

Thus if we write:

$$\left\langle \sum_n \psi_n(x_1)\,\psi_n(x_2)\,\delta(E-E_n) \right\rangle = \rho(E\,;x_1,x_2),$$

it follows that

$$\rho(E\,;x_1+a,\ x_2+a)=\rho(E\,;x_1,\ x_2) \quad . \quad . \quad . \quad (47)$$

and is thus of the form:

$$\rho(E\,;\ x_1-x_2).$$

If the Fourier transform of $\rho(E,x)$ is $\rho(E,k)$, it follows that

$$\langle\sum\sum\delta(E-E_n)\delta(E-E_{n'})D_{nn'}D_{n'n}\rangle=(\hbar^2/m^2)\int k^2\{\rho(E,k)\}^2\,d^3k,$$

so that

$$\sigma=(e^2\hbar^3/m^2)\int\{\rho(E,k)\}^2k_x{}^2\,d^3k. \quad . \quad . \quad . \quad . \quad . \quad (48)$$

This formula does not depend on perturbation theory and is exact except for the factor $(1-\cos\theta)$; it should be exact for isotropic scattering. Also the density of states is given by:

$$n(E)=\int\rho(E,k)\,d^3k. \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

If $\Delta k/k$ is small we may write $\rho(E, k) = \rho_0$ in a range Δk about k_F, and $\rho(E, k) = 0$ otherwise. Carrying out the integration we obtain:

$$\sigma = (e^2\hbar^3/m^2)\rho_0{}^2 S\Delta k\,(4k_F{}^2/3),$$

and for the density of states:

$$n(E_F) = \rho_0 S\Delta k.$$

Using our definition of g (eqn. (46)) we find:

$$n(E_F) = sgS/8\pi^3(\hbar^2 k_F/m),$$

so that

$$\rho_0 = g/8\pi^3\Delta k\,(\hbar^2 k_F/m).$$

It follows that

$$\sigma = Se^2 g^2/12\pi^3\hbar\Delta k.$$

If as before we define the mean free path L by:

$$L = 1/\Delta k,$$

the required formula (45) follows.

It is difficult to extend this method to the particular case of interest here, namely that when $\Delta k/k \sim 1$. Here we may use a method due to Mott (1966, see also Mott and Twose 1961) in which the elements $D_{nn'}$ are evaluated directly. We divide the total volume Ω into elements $\omega = L^3$ in each of which the wave functions ψ_n, $\psi_{n'}$ may be considered coherent. Thus within any volume element ω the wave functions ψ_n will be made up of waves going in all directions, of the form:

$$\psi_n = \sum A_{nk} \exp(ikx).$$

The integral over the volume ω of

$$\int \psi_{n'}{}^* (\partial/\partial x)\psi_n\, d^3x = \Omega^{-1} \sum\sum A_{nk} A_{n'k'} f(K),$$

where $\mathbf{K} = \mathbf{k} - \mathbf{k}'$ and

$$\begin{aligned} f(K) &= \int \exp(-i\mathbf{k}_{n'}\mathbf{r})\frac{\partial}{\partial x}\exp(i\mathbf{k}_n\mathbf{r})\,d^3x \\ &= k_x\omega \qquad KL < 1 \\ &= k_x/K^3 \quad KL > 1. \end{aligned}$$

Assuming all the phases random, the integral over Ω will be $(\Omega/\omega)^{1/2}$ times the integral over ω, so that

$$\left.\begin{aligned} |D_{nn'}|^2 &= (1/\Omega\omega)k_x{}^2/K^6 \quad KL < 1 \\ &= (\omega/\Omega)k_x{}^2 \qquad\quad KL > 1. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (50)$$

We now have to sum over all k, k'. We replace the sum by integrations, both over the Fermi surface and perpendicular to it. This involves multiplying by the factor:

$$(\Omega/8\pi^3)/(dE/dk)^2.$$

The first integration over the Fermi surface gives, using (50):

$$\int |D_{nn'}|^2 dS \simeq k_x^2 \frac{\omega}{\Omega}\left\{\int_0^{1/L} K\,dK + \int_{1/L}^{2k_{\mathrm{F}}} \omega^{-2}\,dK/K^6\right\}.$$

Remembering that $\omega = L^3$, both terms are of order:

$$k_x^2 L/\Omega.$$

Most of D, therefore, comes from values of k, k' such that $|\mathbf{k}-\mathbf{k}'| < 1/L$.

The second integration over the Fermi surface simply introduces the factor S. Thus:

$$\sigma = \mathrm{const}(e^2\hbar^3/m^2)Sk^2 L\Omega/(dE/dk)^2. \quad . \quad . \quad . \quad . \quad (51)$$

Rearranging and putting $\Omega = 1$, formula (44) follows.

All this assumes that $Lk_{\mathrm{F}} \gg 1$ and that g is unity. If this is not so, the two integrations perpendicular to the Fermi surface introduce our factor g^2. But of course the wave functions ψ_n, $\psi_{n'}$ are no longer plane waves. What happens then depends on whether g is less or greater than unity.

In crystalline solids, the case $g \gg 1$ arises with a partly full s-band (for instance) in the tight binding case. Then the integral for $D_{nn'}$ in the important region where $|\mathbf{k}-\mathbf{k}'| < 1/L$, is simply the velocity vector:

$$\int \psi^*(\partial/\partial x)\psi\, d^3x,$$

which (Mott and Jones 1936, p. 265) is proportional to the group velocity $\partial E/\partial k$. Thus in this case the density of states g cancels out from the formula (51) for the conductivity. We think the same would happen for the disordered lattice. If a liquid alkali metal were expanded, one ought to use the formula (44); L will decrease, and eventually when $L \sim \lambda$ bound states *may* well appear and if they do the material will behave as a semiconductor.

For divalent metals, if $g < 1$, however, the matrix elements D cannot *increase* appreciably above k_x. Wave-functions in the solids are of the form (8), and it seems probable that in the liquid they are made up of wave-functions of this kind, so at most

$$|D|^2 \sim k_{\mathrm{F}}^2 + \gamma^2.$$

These arguments then suggest that, when $g < 1$, the factor g^2 does enter into the formula for the conductivity and no compensating large increase of D is expected.

4.7. *The Mean Free Path in the Intermediate Case*

In § 4.6 it has been shown that the conductivity σ is proportional to $e^2Sg^2L/\hbar$, where L is the mean free path. This result is not a consequence of perturbation theory. According however to Edwards (1962), to the second order of perturbation theory:

$$L = L_{\mathrm{Z}}/g^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

where L_Z is calculated as in Ziman's work (§ 4.3). This occurs because $1/\tau$ is proportional to g/τ_Z; the probability of scattering decreases if the density of the (final) states is low; and the analysis introduces another factor g since $L=v\tau$ and v appears as $\hbar^{-1}\, dE/dk$ in fig. 6. The factor g thus cancels out and to the second order of approximation (44) follows.

This cancellation is unlikely to be valid in the case of strong interaction, and the analysis of Faber (1967) does in fact lead to a correcting term. However, it may well be that Ziman's formula for σ gives fair answers, even if the calculated value of L_Z comes out less than the interatomic distance. The true mean free path is L_Z/g^2, and this may be considerably greater than L_Z before localized states occur. This may be the origin of the surprising agreement with experiment obtained by Wilson (1963) in his calculation of the resistivity of solutions of metal in liquid alkali halides under conditions when L_Z as calculated is much less than $1/k_F$ (§ 7.4).

We believe then a theory such as Ziman's may well describe liquid metals and semi-metals surprisingly well; as g drops, L_Z will increase if $|v(q)|^2 a(q)$ has a large maximum somewhat below $q=2k_F$. But probably near the limiting wavelength ($k_F L \sim 1$), g^2 will be the determining factor in the conductivity.

If localized states occur when $g=\frac{1}{2}$ and if kL is then of order unity, the lowest metallic conductivity possible is roughly:

$$e^2 S/48\pi^3 k_F \hbar. \qquad (53)$$

Since $S=4\pi k_F{}^2$, this depends only on the cube root of the number n of electrons per unit volume and is about 200 ohm^{-1} cm^{-1}. If the interaction becomes stronger—or if in discussing divalent metals the distance between atoms becomes greater — the mechanism for conductivity will then go over to hopping so that

$$\sigma=(n\nu e^2 a^2/kT)\exp(-W/kT). \qquad (54)$$

This also depends on $n^{-1/3}$ and, apart from the exponential factor, is of order 1000 ohm^{-1} cm^{-1}. We do not therefore expect any discontinuity in the conductivity. Moreover W will be small as long as the orbitals of the states overlap several others; we should not expect a strong dependence of conductivity on temperature until something near a band gap is formed.

These predictions are examined in § 6.

4.8. *Conductivity Determined by Intercrystalline Barriers*

Many examples exist in the literature where the mobility of electrons is due to potential barriers at grain boundaries; in an n-type semiconductor, for instance, acceptors at the grain boundaries will produce a barrier, so that the d.c. mobility should be governed by a term of the type $\exp(-H/kT)$, where H is the height of the barrier. This mechanism was first suggested by Gibson (1951) and Smith *et al.* (1957, p. 146) to explain the photoconductivity of lead telluride films, though later work suggests that part of the photo-effect may not be due to this cause (Woods 1957). Mueller (1961) however has established that the effect exists in polycrystalline n-type germanium and has measured it in a bicrystal; here a Schottky barrier is formed of height approximately equal to the band width. Jonker (1964) has discussed doped barium titanate in these terms; the barriers disappear below the ferroelectric Curie temperature (for an explanation see Heywang 1963). Grain boundary effects are known to influence the resistivity strongly in NiO and α-Fe_2O_3 (Bosman, private communication). According to Stuke (1964, 1965) barriers play a role in selenium even in single crystals, being formed along sub-grain boundaries or something similar. Such effects may occur in amorphous materials (§ 6.3), either due to Schottky barriers or fluctuations in density.

In such materials we expect the thermoelectric power to be determined by the material between the barriers; a comparison of thermopower and conductivity suggests a very low mobility. The Hall coefficient, on the other hand, will depend on whether the barriers are thick, so that a few electrons are excited to the top of the barrier, or thin, so that electrons penetrate by tunnel effect. In the former case the Hall voltage should be determined by electrons at the top of the barriers, so we should expect large R and normal Hall mobility. In the latter case the Hall voltage is determined by electrons in the bulk of the material, and we expect very low Hall mobilities.

Finally we may mention the work of Weisberg (1962) and Bube and MacDonald (1962) on the existence in certain semiconductors of very large scatterers, rather similar to the barriers discussed here.

§ 5. Optical Properties

In a study of electrons in liquid and amorphous materials, the main interest in measurements of the optical properties lies in the wide applicability of the Drude formula for liquid metals, in deviations from it for semi-metals such as tellurium and in investigations of the tail of the absorption band due to disorder.

We shall throughout discuss our results in terms of the quantity which is the real part of the a.c. conductivity; the imaginary part is linked to it by the Kramer–Kronig relations. The Drude formula, valid for free electrons, is:

$$\sigma(\omega)=Ne^2\tau/m(\omega^2+\tau^2). \qquad (55)$$

where N is the number of free electrons per unit volume and ω the time of relaxation. The quantity $\sigma(\omega)$ must necessarily satisfy the sum rule:

$$\int_0^\infty \sigma(\omega)\,d\omega=\pi e^2N/2m. \qquad (56)$$

The standard Kramers–Heisenberg dispersion theory gives for $\sigma(\omega)$:

$$\sigma(\omega)=\frac{2\pi e^2\hbar^2}{m\Omega\omega}\int_0^\infty \{f(E)-f(E+\hbar\omega)\}n(E)n(E+\hbar\omega)|D(E,\omega)|^2\,dE, \qquad (57)$$

where f is the Fermi–Dirac distribution function and

$$D(E,\omega)=\int \psi^*_{E+\hbar\omega}(x)\,\frac{\partial}{\partial x}\,\psi_E(x)\,d^3x.$$

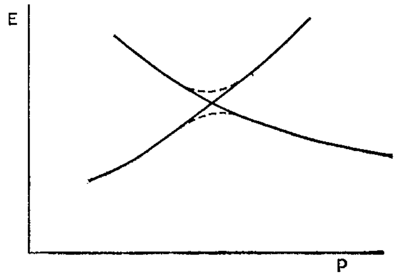
The notation is due to Faber (1966). As Faber points out, as $\omega\to 0$ and if $kT \ll E_{\mathrm{F}}$, this reduces to:

$$\sigma(0)=(2\pi^2e^2\hbar^3/m^2\Omega)\{n(E_{\mathrm{F}})\}^2\,|D(E_{\mathrm{F}},0)|^2,$$

which is identical with the Kubo–Greenwood formula (42) for the d.c. conductivity. Both these formulae should be averaged over all configurations of the amorphous or liquid lattice.

We shall first ask what happens to $\sigma(\omega)$ when the initial and final states are localized. Contributions to $\sigma(\omega)$ will only occur when, accidentally, two states, of which the orbitals overlap, have energy differing by exactly $\hbar\omega$. Of course when this occurs the absorption coefficient is infinite (if one calculates it with neglect of line width), so on averaging over all configurations one obtains a finite value of $\sigma(\omega)$. But the absorption process takes place between very few pairs of states.

Fig. 10



Schematic representation of energy E as a function of a configurational parameter p for two localized states.

At first sight it might seem that the same argument could be applied to the d.c. conductivity, predicting a small transient current as electrons jump between states which accidentally have the same energy and whose orbitals overlap. But this is not so. Two overlapping states cannot have the same energy. Figure 10 represents schematically the energies of two overlapping states as a function of some parameter p representing the positions of the atoms. The two states will combine, giving eigenvalues of the energy as shown by the dotted lines. If both orbitals fall off as $\exp(-r/a)$, and the orbitals are R apart, the splitting ΔE will be of order:

$$\Delta E=E_0\exp(-R/a),$$

where E_0 is the band width.

We can deduce the behaviour of $\sigma(\omega)$ for small ω. Suppose there are n localized states per unit volume in the range E_0. Then the absorption for frequency ω will be proportional to:

$$N\int_{R_0}^{\infty} \exp(-2R/a)\, R^2\, dR,$$

where R_0 is given by:

$$\hbar\omega \sim \Delta E.$$

The result is clearly proportional to ω^2, so

$$\sigma(\omega) = \text{const.}\, \omega^2$$

for small ω, if the initial and final states are localized.

Halperin (1967) has given a direct proof that $\sigma(0)=0$ for the one-dimensional case. He points out that one may write:

$$\langle n\,|p\,|\,n'\rangle = (im/\hbar)\langle n\,|x-z\,|\,n'\rangle(E_n-E_{n'}),$$

where z is any point. It follows that

$$\sum_{n'} \frac{|\langle n\,|p\,|\,n'\rangle|^2}{(E_n-E_{n'})^2} = \frac{m^2}{\hbar^2}\langle n\,|(x-x_n)^2|\,n\rangle,$$

where

$$x_n = \langle n\,|x\,|\,n\rangle.$$

If states are localized, $\langle n\,|(x-x_n)^2|\,n\rangle$ is finite; otherwise it tends to zero as the volume increases. Thus if we define

$$F(E, E+\hbar\omega) = \Omega\sum\sum|\langle n\,|p\,|\,n'\rangle|^2\,\delta(E-E_n)\,\delta(E+\hbar\omega-E_{n'}),$$

where Ω is the volume of the specimen, it follows that $\int (F/\omega^2)\,d\omega$ is finite and thus that F vanishes at $\omega=0$. Therefore the conductivity given by the Kubo–Greenwood formula vanishes as $\omega \to 0$.

Faber (1966, 1967) has given a proof that (57) leads to the Kubo formula to the second order of perturbation theory, and that the cancellation of the factor g^2 occurs in $\sigma(\omega)$, just as it does for $\sigma(0)$. The deviations from the free-electron formula observed for mercury at very low frequencies (Faber 1966) probably cannot be explained through the factor g, as was attempted by Mott (1966). On the other hand, in the range where $L \sim \lambda$, then, just as for $\sigma(0)$, one would expect the factor g^2 to have an effect on the absorption coefficient. Thus we expect for $\sigma(\omega)$ to appear as in fig. 11. The curves shown refer to the following cases.

(*a*) The Drude formula.

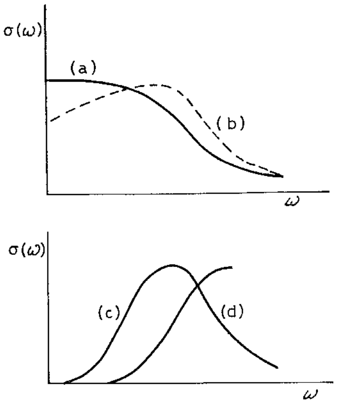
(*b*) A situation with short mean free path and low $n(E_F)$—such as in tellurium (§ 6). The curve must rise above the Drude formula because of the sum rule (56). This may be ascribed either to values of $n(E)$ greater than the free-electron value, or to the form of the wave-functions; if those in the initial state are mainly s-like and in the final state p-like this will enhance the absorption.

(*c*) Shows the situation when E_F lies in the region of localized states, but the states lie close enough together in space for significant overlap.

(*d*) Shows the case of an insulator (such as fused quartz), with a real energy gap containing a negligible number of localized states which overlap.

We have not discussed exciton formation; if the final states are localized, obviously the concept does not apply, though the absorption tail will be shifted towards longer wavelengths by the Coulomb attraction between the electron and hole.

Fig. 11



$\sigma(\omega)$ as described in text: (*a*) Drude formula, weak interaction, (*b*) strong interaction (e.g. liquid tellurium), (*c*) liquid semiconductor, with localized states overlapping, (*d*) liquid insulator.

Finally it is worth mentioning that a number of examples exist in the literature of absorption measurements in liquid or amorphous materials where the absorption spectrum differs little from that of the crystal. Germanium and tellurium are discussed in this connection in § 6.12; Phillipp (1966) has discussed amorphous quartz and Beaglehole (1965) liquid xenon.

§ 6. OBSERVED BEHAVIOUR OF NON-CRYSTALLINE MATERIALS

6.1. *Introduction*

The available experimental evidence will be discussed under the following headings.

In § § 6.2, 6.3 and 6.4 we treat materials which are definitely non-metallic in the amorphous and liquid states. Under this heading we discuss

(*a*) Measurements of drift mobility in which electrons are injected into a non-crystalline insulator.

(*b*) The behaviour of amorphous semiconductors and insulators.

(*c*) The behaviour of liquid semiconductors and insulators. These are in principle more complicated than amorphous materials because the structure and hence $n(E)$ will change with temperature. We confine ourselves in this section to intrinsic conduction; electronic conduction due to sodium in ammonia or excess potassium in liquid KCl is treated in § 7.

In §§ 6.5, 6.6, we treat amorphous metals and liquid metals, and in § 6.7 materials which appear to fall between the two categories.

6.2. *Drift Mobilities*

Experiments which establish the drift mobility directly are of particular interest. As we have seen, the Hall mobility is difficult to interpret for hopping and even for non-hopping motion if L is comparable with λ. On the other hand, measurements of the drift mobility may measure *either*

(*a*) Motion by hopping only, as in impurity conduction.

(*b*) Motion in a conduction band (i.e. the unshaded range of energies in fig. 7), limited by trapping in localized states.

(*c*) Mobility in a conduction band when trapping is negligible. Various examples will be described below.

Argon. Schnyders *et al.* (1965) have measured mobilities μ of injected electrons in liquid argon. Oxygen forms effective traps and if enough O_2^- ions are present, it is their mobility rather than that of the electron that is observed. An oxygen content less than $10^9\,\mathrm{cm}^{-3}$ is required in order to observe the drift mobility of the electrons. The mobilities are then large (*ca.* 400 $\mathrm{cm}^2/\mathrm{v\,sec}$), and *decrease* with increasing temperature. There is thus no sign of trapping. If we use our criterion that localized states appear in the tail of a conduction band when $L \sim \lambda$, this is not surprising. The mean free path is *ca.* 10^{-6} at 100 °K, so if we set (in centimetres):

$$L = 10^{-6}\,(T/100)^{-3/2}, \quad \lambda = 3 \times 10^{-7}\,(T/100)^{1/2},$$

we see that the two are comparable at 30 °K, below the temperature of liquid argon. Schnyders *et al.* found a rough agreement between their results and the mean free path calculated as in § 4.2, and Cohen and Lekner (1967) and Lekner (1967) have examined the problem in detail, solving Boltzmann's equation for hot electrons and determining the scattering by argon atoms including the long-range polarization potential.

Recently Miller and Spear (1967) have measured drift mobilities of electrons in solid argon and find values close to those for the liquid; holes are not mobile.

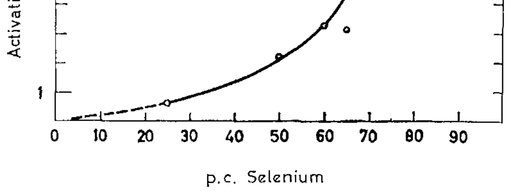
Selenium. Spear (1957, 1960) has made measurements of transit times for electrons and holes in amorphous selenium. He finds that the mobility is controlled by traps, which for electrons are 0·25 ev below the conduction band and for holes 0·14 ev. For the holes the trapping acceptor states are present at a concentration of about $10^{20}\,\mathrm{cm}^{-3}$ and are present in both the amorphous and the crystalline material; they must therefore be due to polaron formation rather than to disorder.

Chalcogenide glasses. Hirsch (1966) has produced electrons by bombardment in these materials and finds very low drift mobilities of the order 3×10^{-7} for electrons 3×10^{-9} for holes. Hirsch considers that immediately after illumination the current is carried by electrons, which however are soon captured by deep traps, so that after a longer time the current is carried by a larger concentration of less mobile holes; these eventually recombine with the trapped electrons. He estimates that these deep traps are present in a concentration of 1 per 10^4 (10^{18} molecules/cm^2).

6.3. *Amorphous Semiconductors; Tellurium, Germanium and Selenium*

There has recently been a considerable amount of work on the properties of evaporated films of these materials, notably by Grigorovici in Bucharest, Stuke in Karlsruhe and Tauc in Prague. Amorphous films of these materials retain the coordination number of the crystalline state (Richter and Breitling 1958); amorphous germanium does not show the high coordination number and metallic conductivity of the liquid. All these materials are much worse conductors in the amorphous than in the crystalline state; it was to explain this fact that Banyai (1964) introduced the concept of localized states, though we suggest in this paragraph that there are difficulties in the way of this explanation and that another may be preferable.

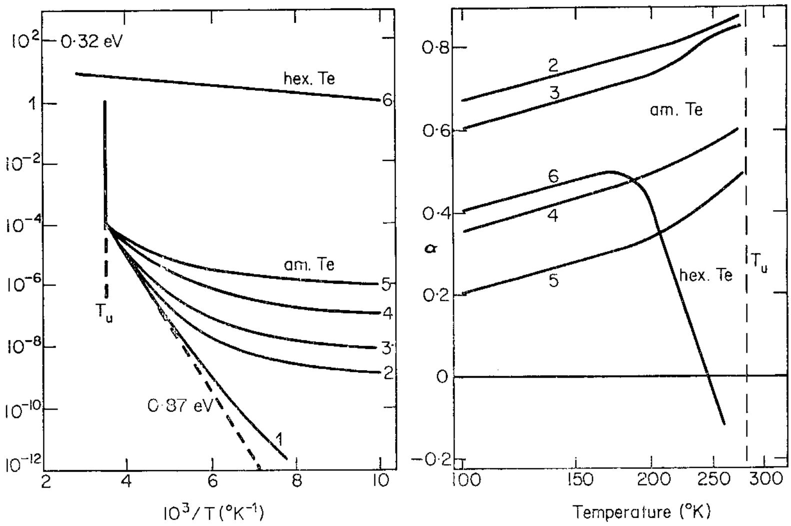
Fig. 12



Activation energy for extrinsic conduction in crystalline Se–Te (Stuke).

We contrast first selenium and tellurium, normally p-type conductors. The abnormal properties of selenium have been known for many decades, in particular the dependence of resistivity on the electric field strength. According to Stuke (1964, 1965) this is due to the presence of surfaces in the crystal containing donors which set up Schottky barriers whose height is sensitive to the field (cf. § 4.8); their number and height is increased by cold work. No such effect has been observed in tellurium but if the barriers exist they must be much lower, as the energy gap is 1·85 ev or a little bigger for Se and only 0·32 ev for Te (Stuke 1967). For extrinsic conductivity the activation energy for tellurium is extremely small and is about 10^{-1} ev for selenium; fig. 12 shows the activation energies for extrinsic conduction for a series of Se–Te alloys. The dependence of the conductivity on direction is also greater for selenium than for tellurium, $\sigma_{\parallel}/\sigma_{\perp}$ being 3·3 and 1·9 respectively; Stuke and Weiser (1966) have used the Franz–Keldysh effect to show that for selenium the effective mass is 6·5 times larger perpendicular to the axis than parallel to it.

Fig. 13

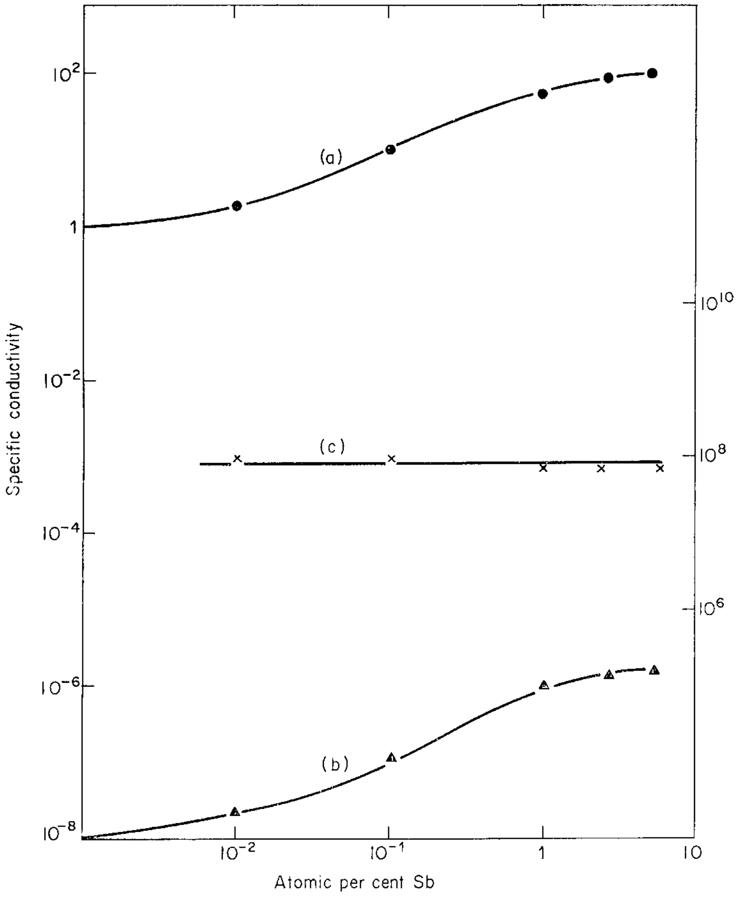


Conductivity σ ($\text{ohm}^{-1}\ \text{cm}^{-1}$) and thermopower α (microvolt/degree) of amorphous tellurium as a function of T. For the thermopower the temperature is plotted logarithmically (Keller and Stuke). Curves 1–3 are for different rates of evaporation, 4 and 5 for doping with Sb.

Turning now to the amorphous films of tellurium investigated by Keller and Stuke (1965), by Stuke (1967), and by Stuke and Cauer (unpublished), fig. 13 shows the conductivity as a function of temperature. It will be noted that the conductivity of the amorphous material is several orders of magnitude lower than for the crystalline, and that it apparently consists of an 'intrinsic' and 'extrinsic' part. The curves 1–5 refer to different doping or rates of evaporation. Stuke (1967) has also found that amorphous tellurium can be 'doped' by antimony, and the number of carriers (holes) thereby introduced is the same as in hexagonal tellurium; this is shown in fig. 14, in which the conductivity is plotted against concentration of antimony for the crystalline and amorphous materials, and it will be seen that $\sigma_{\text{polycryst}}/\sigma_{\text{amorp}}$ remains constant.

It follows from this result that any localized states introduced into the energy gap (as in fig. 7) by the disordering must have very low concentration (*ca.* 10^{-5} per atom); unlike the glasses discussed by Gubanov (see below), these materials do respond to low concentrations of doping, and at 100°K the number of 'free' carriers is equal to the concentration of antimony. But the values of the conductivity show that the carriers in the amorphous phase have a temperature-activated mobility which is much smaller than for the crystal.

Fig. 14



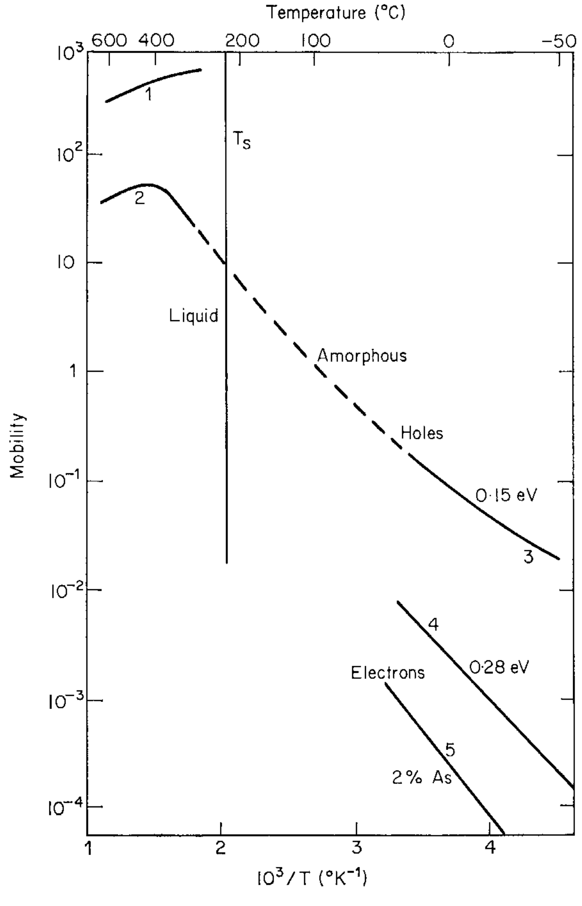
Conductivity ($\text{ohm}^{-1}\ \text{cm}^{-1}$) against concentration for tellurium doped with antimony at 100°K (Stuke and Weiser). (*a*) polycrystalline, (*b*) amorphous, (*c*) ratio.

The results on the thermopower α shown in fig. 13 show that at low temperatures

$$\alpha = -(k/e)\ \tfrac{3}{2} \ln T + \text{const.}, \qquad \qquad (58)$$

both for amorphous and polycrystalline tellurium; doping with antimony only changes the constant. Since (cf. § 4.4) the factor $\frac{3}{2}$ is a consequence of a parabolic band form, it seems that the density of states near the bottom of the valence band is not appreciably altered by the amorphous structure. This seems to us hardly compatible with localization, unless the radius of the localized orbital is very large, in which case one would hardly expect an appreciable activation energy.

Fig. 15

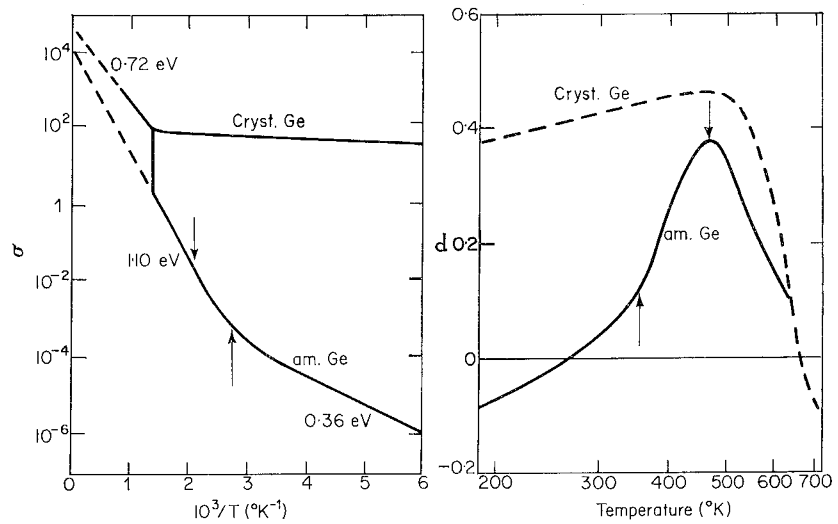


Drift mobility (cm^2/v sec) of electrons and holes in liquid and amorphous selenium; activation energies are marked.

An alternative hypothesis for the low mobility is that Schottky barriers due to surfaces with a high density of donors exist in these amorphous materials, of the kind which Stuke (1964, 1965) has shown to exist in crystalline selenium and which are familiar in polycrystalline materials (§ 4.8). A much higher barrier is possible in amorphous than in crystalline tellurium, because the energy gap is much wider in the former (see below). Alternatively, barriers may be due to changes in the density.

We now discuss the magnitude of the extra activation energy for the mobility in the amorphous state—without resolving the question of its cause. For tellurium the activation energy for the intrinsic range is $E_G = 0{\cdot}87$ ev, contrasted with 0·32 ev in the crystalline state. Stuke however has found an increase in $h\nu$ for the optical absorption edge by 0·4 ev, which he ascribes to a widening of the band gap due to the increase in the distance between the chains in the amorphous state; the energy gap in tellurium is known to decrease under pressure (Blum and Deaton 1965). If then the intrinsic part of the curve is due to the excitation of holes from the conduction band to the *non-localized* part of the valence band—or *above* the Schottky barriers if they provide the correct explanation —then the width of the former or the height of the latter is 0·15 ev.

Fig. 16



Conductivity σ (ohm^{-1} cm^{-1}) and thermopower α (microvolt/degree) of amorphous and crystalline germanium. Activation energies are marked (Grigorovici *et al.*).

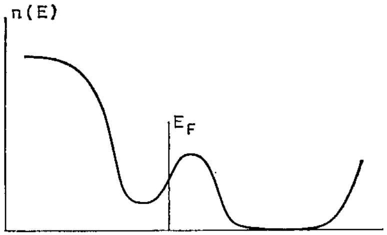
Amorphous selenium can be obtained by supercooling as well as by evaporation and—unlike tellurium—the chains persist in the liquid phase. Figure 15 shows results of Spear (1960) and of Hartke (1962) and unpublished work of Gobrecht *et al.* on the drift mobility of electrons and holes in the amorphous material, suggesting that there may be continuity between the amorphous and liquid states, and showing a strong temperature dependence as for tellurium.

The results of Grigorovici *et al.* (1964) on the conductivity[†] and thermopower of amorphous germanium films are shown in fig. 16; the general behaviour of the conductivity of evaporated films is similar to that for tellurium, but Tauc *et al.* (1966) find no change in the absorption edge on going to the amorphous state, so the marked increase of the band gap observed for tellurium does not occur. One would expect amorphous germanium to contain a high concentration of broken bonds and that this would produce a broad band of acceptors (compare Heine 1966), which are probably the main source of mobile holes in the extrinsic range. However, the change of sign of the thermopower at low temperatures, not found in tellurium, introduces an interesting point. In tellurium we have supposed that current is carried by a non-degenerate gas of holes and that a formula (§ 4.4)

$$\alpha S = (k/e) \ln (N_{\mathrm{p}}/n) + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (59)$$

can be used, where e is the *positive* charge of the hole, whether motion is by hopping or not. The form of N_{p}, proportional to $T^{3/2}$, depends on the existence of a parabolic band form. For these germanium films, on the other hand, the concentration of acceptors is about $10^{19}\,\mathrm{cm}^{-3}$ (see below) and this should be ample to allow hopping from one to another or in the crystalline phase for the formation of a degenerate gas. If the donors form a separate band or peak in the density of states curve, as in fig. 17, and if there is some compensation so that the Fermi energy lies as shown, then a change of sign of α is to be expected, whether the states are localized or not, and whether the gas is degenerate or not. We think that this change of sign shows simply that conduction is within an impurity band in which $n(E)$ increases with E at the Fermi level, but does not say anything about the mechanism of conduction.

Fig. 17



Suggested density of states for amorphous germanium.

Tauc *et al.* (1966) have investigated the optical constants of amorphous germanium films of thickness between 400 and 4000 Å. In the range of characteristic absorption (0·8 ev to 10 ev) the fine structure of the optical

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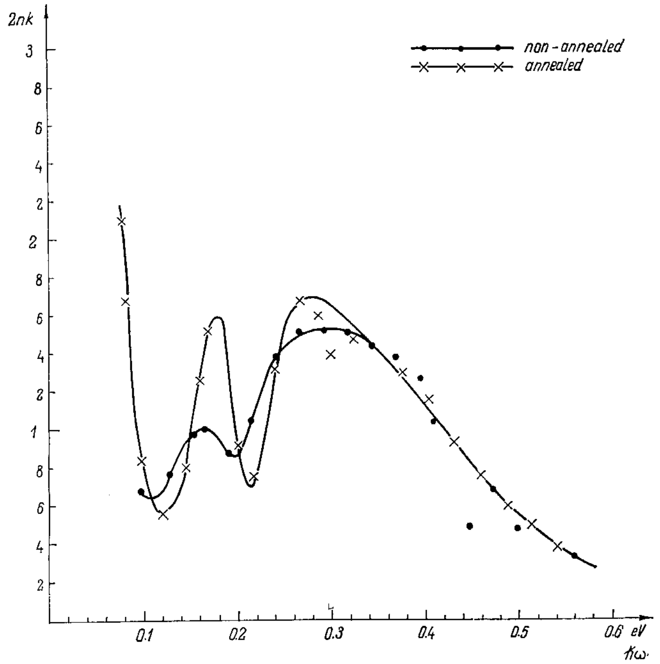
[†] Suhrmann *et al.* (1963) show that the effect of an ultra high vacuum has little effect on the conductivity.

constants is smeared out. Tauc *et al.* deduce that there is little change in the band form but the k-selection rule breaks down due to the disorder. Of particular interest, however, is the infra-red absorption in the range 0·1 to 0·4 ev. This is shown in fig. 18 for the amorphous and annealed (crystalline) states. In the crystalline state this fine structure is due to k-conserving transitions of electrons from the lower branch of the valence band to the two upper branches. We must deduce that in the amorphous material the states near the top of the valence band are made up of Bloch functions with a rather small spread of energy.

Fig. 18



Infra-red absorption of amorphous and annealed (crystalline) germanium films (Tauc *et al.*).

This apparent retention in the amorphous state of a k-vector sufficiently well-defined to keep the three branches of the valence band seems hardly comparable with the existence of states so localized as to give hopping with a reasonable activation energy. It is possible that in germanium also the states are not localized or only very weakly so, and the explanation of the low conductivity of the amorphous material is Schottky barriers. Just how they are formed is not clear. In crystalline germanium barriers at grain boundaries are formed only in n-type material (for references see Heine 1966).

Stuke (private communication) has suggested that particularly in tellurium barriers may be due to fluctuations in density; there may for instance be regions in which all bonds are saturated, separated by boundaries where this is not so, so that near these boundaries the density is low. For most semiconductors (but not for germanium) the forbidden band widens when the density decreases, so one would expect barriers to be set up both for movement of holes *and* of electrons (Schottky barriers would affect majority carriers only). If, as one would expect, the barriers were higher in the conduction than in the valence band, this would account for the predominantly p-like conduction in the intrinsic range. The mobilities for amorphous selenium (fig. 15) confirm this. At low temperatures tunnelling through the barriers may be important.

6.4. *Chalcogenide Glasses*

The electrical properties of these materials have been studied in detail, particularly by the Leningrad school. Kolomiets (1964) has reviewed this work in English, and a more recent collection of reprints (Myuller 1966) has been translated. Experimental work from the Bell Laboratories (Pearson *et al.*), and unpublished work from the University of Sheffield (Owen) and from the C.E.G.B. Laboratories (Edmond 1966) are referred to in this section.

The Leningrad school emphasizes:

(*a*) The glassy materials usually have conductivities many orders of magnitude smaller than the crystals (cf. for instance, fig. 11 on p. 716 of Kolomiets' review).

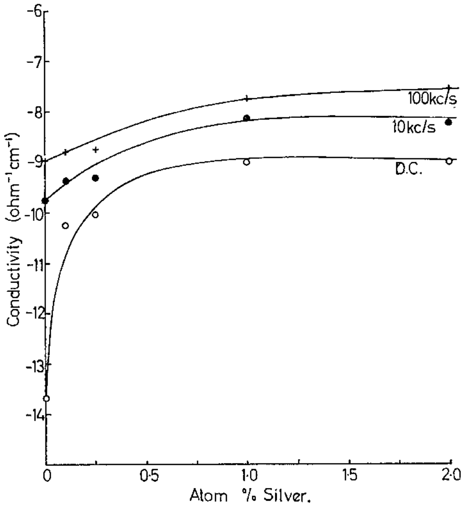
(*b*) They appear to show a single activation energy E for conduction, lying in the range 1–2 ev, suggesting intrinsic conductivity rather than hopping or a transition from intrinsic to extrinsic. Edmond (1966) remarks that in As_2Se_3 the strong absorption at 1·92 ev fits fairly well with the observed conductivity of the form $\sigma_0 \exp(-E/kT)$ with $E \simeq 1{\cdot}1$ ev if this is intrinsic, but is difficult to reconcile with a hopping mechanism.

(*c*) In general impurities have much less effect on the conductivity than in the crystalline state, though Owen (private communication) finds that the effect of silver is large, as is also that of copper according to Danilov and Myuller (1962; see Doinikov and Borisova on p. 59 of Myuller 1965). These authors find that 19 at. % of copper reduces the activation energy of conduction in As_2Se_3 from 1·83 to 0·87 ev. They have investigated the effect of from 5 to 10 at. % of Be, Mg, Ca, Zn and other metals in As_2Se_3, finding a change in σ at 20°c by less than 10. Owen finds that the large effect of silver is not shown for a.c. at comparatively low frequencies, as shown in fig. 19.

As regards the frequency effect, glasses of composition $As_2Se_{3-x}Te_x$ are known to conduct better as x increases, and Edmond remarks that the frequency effect diminishes as the conductivity increases.

The Leningrad school has suggested that the localized state model described in § 4.1 may explain the lack of extrinsic conduction due to impurities (Gubanov 1963). If there is a pseudo-gap (fig. 7) 1–2 ev wide but with a few localized states within the gap, some occupied and some empty, then the addition of impurities which can contribute electrons will have no effect but to shift the Fermi level slightly. If the localized states are too far apart to allow hopping, so that conduction is intrinsic, they will have little effect on the conductivity. But it is difficult to explain the small effect of *large* amounts of most impurities in this way. We think that in glasses the impurities which produce little effect on σ must use all their valence electrons in bonds with surrounding atoms or ions, modifying the local coordination number to make this possible; they would not then act as donors or acceptors.

Fig. 19



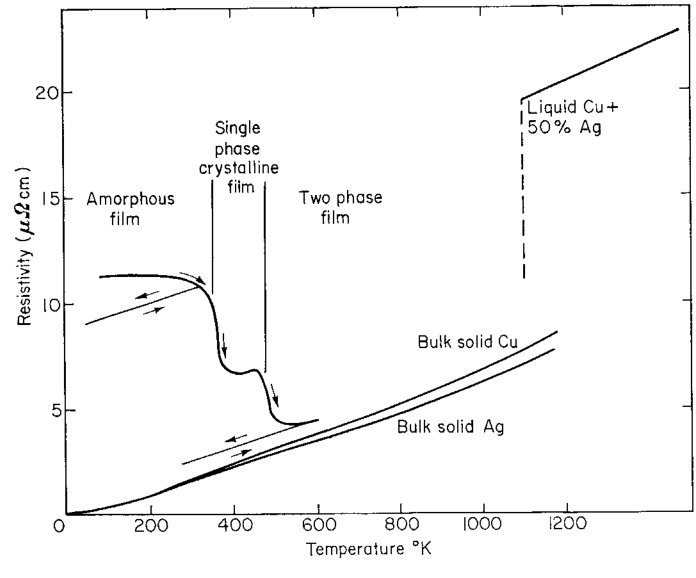
Conductivity of glassy As_2S_3 as a function of Ag concentration (Owen *et al.*).

The enhanced resistance in the amorphous state is perhaps due to the same reasons as in amorphous tellurium, namely expansion of the lattice with consequent increase in the energy gap, and barriers at regions of abnormally low density. The barriers give a qualitative explanation of the facts recorded in fig. 19, namely the very low frequency at which the rise in conductivity begins. Presumably copper and silver act by removing the barriers through some unknown mechanism. All these materials show p-type thermoelectric power, suggesting that the barriers are higher in the conduction than in the valence band. However, Pearson (1964) considers that the negative Hall coefficient *may* be due to the presence of regions that have crystallized and therefore have high conductivity. We feel that too little is known about the nature of the barriers (if they exist) for further speculation about the Hall constant to be profitable at this stage.

6.5. *Amorphous Metals*

Metastable alloy films of a number of binary alloy systems can be prepared by the simultaneous vapour deposition of two components onto a cold substrate (Mader *et al.* 1963, Mader 1965); the condition for this to be possible is in general a difference in the atomic radii in excess of 10%. The films are stable up to about 0·3 T_M, where T_M is the melting temperature. The results are of interest because they show that the alloy films at low temperatures have resistivities close to those of the liquid, no rise in ρ is observed and so experimental evidence is available that the states at the Fermi surface are *not* localized. Figure 20 shows some results for Cu + 50% Ag. An interpretation of $d\rho/dT$ in terms of the effect of phonons on $a(q)$ has not yet been attempted.

Fig. 20



Resistivity of amorphous films of Cu + 50% Ag evaporated at 80°K as a function of temperature showing reversible and irreversible behaviour due to annealing (Mader).

Similar results have been obtained by Buckel and Hilsch (1954), Buckel (1954) and Barth (1955) on evaporated bismuth films which according to their results and those of Richter and Steeb (1959) are amorphous. The resistivity is close to that of the liquid, as is the Hall coefficient. Amorphous bismuth and its alloys show superconductivity (for references to recent work see Shier and Ginsberg 1966). The papers quoted above describe results also for tin and other metals.

Duwez *et al.* (1965) have obtained an amorphous phase of palladium–silicon alloys with 15–23 at. % Si by rapid cooling from the melt; the resistivity has been measured down to 2°K and shows little change between this temperature and 400°K.

6.6. *Normal Liquid Metals*

By 'normal' I mean a liquid metal in which the mean free path L is long compared with the interatomic distance. For such metals, as explained in § 4.2, Ziman's theory of nearly free electrons should be valid. There have been other reviews of the properties of such metals (Cusack 1963, Ziman 1967) and this article will only touch on them briefly.

Table 2 (partly from Cusack 1963) gives the values of the mean free paths deduced from the observed resistivity at the melting point and the free-electron formula (§ 4.4). It will be seen that in many metals L is quite large, but in some it is small enough to make deviations from the free-electron theory plausible.

Table 2

	Li	Na	Cu	Zn	Hg	Ga
n L	1 45	1 157	1 34	2 13	2 7	3 17
	Ge	Sn	Pb	Sb	Bi	Te
n L	4 11	4 10	4 6	5 4	5 4	6 0·9
	InSb	GaSb	CdSb	PbTe	HgTe	
n L	4 8	4 7	4 3	5 0·5	4 0·3	

Mean free path L in ängstroms for some metallic liquids from the observed conductivity and formula (45). n is the number of electrons per atom.

There is a large body of work in which the absolute value of the resistivity or thermoelectric power is measured for a metal or alloy and compared with values calculated from estimated pseudopotentials $v(q)$, such as those of Animalu and Heine (1965). References will be found in the papers by Ashcroft and Lekner (1966), already quoted, Animalu (1967), Harrison (1965), Ziman (1967) Halder *et al.* (1966), and Greenfield (1966). It is not our aim in this article to discuss the methods of estimating the Fourier transform of the pseudopotential; we remark only that the zero q_0 in the pseudopotential (fig. 33) is of decisive importance in determining the absolute value of ρ, particularly for the divalent metals. For mercury different models give a variation of ρ_{calc} calculated from theoretical values of $v(q)$ at present available by more than 2.

For divalent metals in particular, and intermetallic compounds, etc., for which the resistivity comes from the peak in $a(q)$, we can see how strongly ρ depends on q_0 by representing the peak by $a(q) = A \exp\{-(q-q_1)^2/\sigma^2\}$ and evaluating the integral:

$$\int_{-\infty}^{\infty} (q-q_0)^2 \exp\{(q-q_1)^2/\sigma^2\}\, dq\,,$$

which should give a fair measure of the resistivity if $2k_F$ lies to the right of the peak. The integral is proportional to:

$$\sigma^3 + 2\sigma(q_1-q_0)^2,$$

so the resistivity is doubled if q_0 is shifted from the peak $(q=q_1)$ by $\sigma/\sqrt{2}$. The sensitivity of the resistivity of mercury to alloying may well be due to shifts in q_1 (cf. § 6.8).

6.7. *Liquid Semiconductors, Semi-metals and Intermetallic Compounds*

We discuss in this section materials which are semiconductors or semi-metals in the crystalline state and which show low conductivity (below 1000 ohm^{-1} cm^{-1}) and for which $d\sigma/dT$ is normally positive. This does not include silicon, germanium and the 3–5 compounds because they are normal metals in the liquid state.

It is characteristic of liquids, of course, that $a(q)$ will change with temperature, so the interpretation of electrical properties may be more complicated than for amorphous films or glasses. A positive value of $(d\sigma/dT)_V$ does *not* necessarily mean hopping or semiconductor behaviour; an early success of Ziman's work (§ 4) was to explain these positive values of $d\sigma/dT$ for divalent metals in terms of the temperature variation of $a(q)$. But conversely we can predict that if σ lies below the critical value σ_0 discussed in § 4.6, conductivity should be by hopping and $d\sigma/dT$ should always be positive. Our ignorance of the value of g, for which localized states occur, makes it impossible to estimate g accurately; if $g = \frac{1}{2}$, a figure in the range 200–1000 ohm^{-1} cm^{-1} may be taken. Table 3, kindly compiled for this article by Dr. Allgaier† shows some typical materials in this class for which σ and $d\sigma/dT$ have been measured. The table does not show any materials for which σ lies below 1000 ohm^{-1} cm^{-1} as having negative values of $d\sigma/dT$, except possibly FeS, for which in the experiments of Argyriades *et al.* (see p. 101) there seemed some doubt as to whether the composition changed with T.

Some of these materials will now be discussed in greater detail. The Hall coefficient and conductivity of liquid tellurium are shown in fig. 21 as measured by Tièche and Zareba (1963). The conductivity lies near the borderline; the Hall coefficient is two or three times larger than one would expect with six free electrons. X-ray evidence from Buschert *et al.* (1955) shows that for liquid selenium the radial distribution shows a peak at 2·9 Å corresponding to a bond length of 2·86 Å in the solid; these authors deduce that the chains dissociate as the temperature is raised. Since

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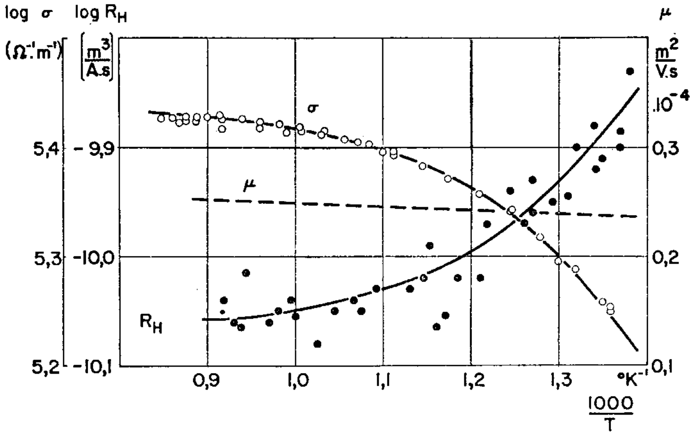
† See also Mott and Allgaier (1967).

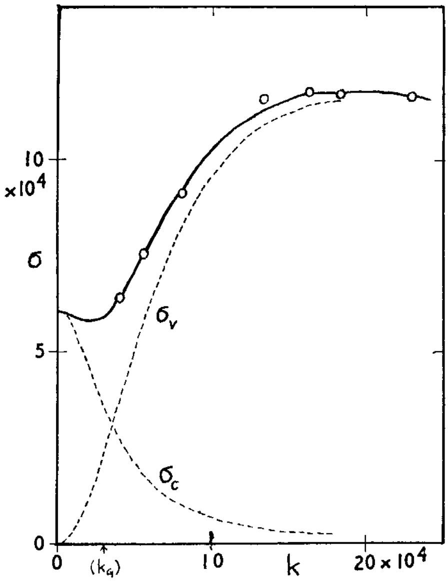
tellurium has very low conductivity in the liquid state, the band gap characteristic of the solid must persist and $n(E_F)$ must be zero or very low. For tellurium with broken chains we should expect a strong minimum in $n(E)$ at E_F, the factor $g\,(=n(E_F)/n(E_F)_{\text{free}})$ rising with T.

Fig. 21



Conductivity σ and Hall coefficient R_H of liquid tellurium as a function of T. The Hall mobility is also shown (Tièche and Zareba).

Fig. 22



Optical absorption $\sigma(\omega)$ for liquid tellurium (Hodgson). k is the wave-number in cm^{-1}; the dotted curves are explained in Hodgson's paper.

Table 3. Properties of liquid semiconductors and semi-metals at or near the melting point. σ is the conductivity in (ohm-cm^{-1})

Material	σ	$d\sigma/dT$	Ref.
Ge	28000	−	14
InSb	17000	−	14
GaSb	16000	−	14
AlSb	12000	−	14
Tl_3Sb	11900	−	19
Tl_3Bi_5	7200	−	19
$CoTe_2$	6000	−	17
Ni_3S_2	5200	−	8
NiS	5100	−	10
CdSb	5000 5200	+	11 18
ZnSb	4200 5200	+	17 11
Co_4S_3	4100	−	8
Bi_2S_3	3400	−	10
Bi_2Te_3	2800 3400	+	11 17
Sb_2Te_3	1800 2000 3500	+	11 3 15
Te	1800 2000	+	6 12
$NiTe_2$	1400	−	17
SnTe	1400	+	9
PbTe	1100	+	17
Bi_2Se_3	900	+	17
GaTe	700	+	5
HgTe	630	+	17
$FeTe_2$	400	+	17
PbSe	400	+	17
FeS	400	+	1
TlTe	330	+	7, 19
Cu_2Te	200 500	+	17 9
Cu_2Se	200	+	17
Ag_2S	200	+	8
FeO	180	+	4
Ag_2Te	150	+	9
Tl_2Te	70	+	7
Cu_2S	50	+	8
Te_8Se_2	40	+	6
CdTe	40	+	13
ZnTe	40	+	14
HgSe	25	+	17
Tl_2Se_3	1·6	+	19
TlSe	1·1	+	19
TlS	10^{-1}	+	19
Tl_4S_3	$6{\cdot}5\times10^{-3}$	+	19
Tl_2S	10^{-3}	+	17
Bi_2O_3	5×10^{-5}	+	17
Se	10^{-8}	+	2, 16

Tièche and Zareba discuss their measurements of the Hall coefficient in terms of ' partial ionization ' of the chains. We are not clear that this is a meaningful concept for a degenerate electron gas. Perhaps the measurements should be interpreted empirically as showing that, for short mean free path, a low density of states at the Fermi energy may give large Hall coefficient.

Figure 22 shows measurements of the optical absorption of liquid tellurium due to Hodgson (1963). These may be interpreted as giving experimental evidence for a low density of states at the Fermi energy (compare § 5 and fig. 11).

We turn now to compounds. Among materials comparable with liquid tellurium in their properties, Enderby and Walsh (1966) have measured conductivities and Hall constants of CdSb, ZnSb, Bi_2Te_3, Sb_2Te_3; for these the conductivity is that of a poor metal and rises slightly with temperature (probably due to the disappearance of a minimum in $n(E)$); the results are shown in fig. 23. The Hall constants, though not corresponding to the number of electrons in outer shells, are of metallic order of magnitude. They also show more variation with temperature. No theoretical interpretation has been offered, though here again we see that, if $L \sim \lambda$, substantial deviations for the free electron value can occur.

Among liquids with conductivities about ten times smaller, Cutler and Mallon (1962, 1965, 1966) have measured the properties of liquid solutions

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References to Table 3 (references not given here when they appear in the list of references at end)

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11. Enderby, J. E., and Walsh, L., 1966.
12. Epstein, A. S., Fritzsche, H., and Lark-Horovitz, K., 1957, *Phys. Rev.*, **107,** 412.
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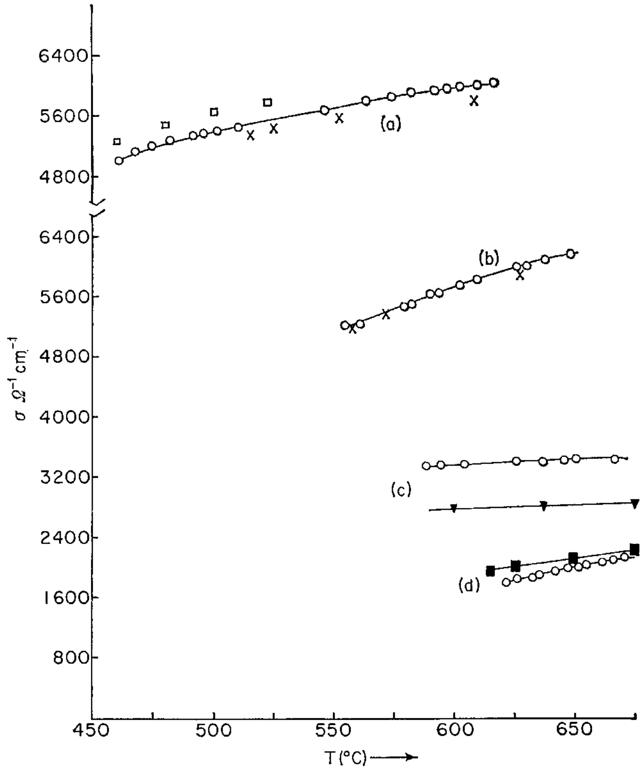
of thallium with tellurium. Results are shown in fig. 24, suggesting that conductivities of these compounds are very much on the borderline between the metallic and non-metallic behaviour. Enderby and Walsh (*loc. cit.*) have measured the Hall constant of stoichiometric liquid Tl_2Te and found that it is negative and less by a factor 10 than for the more metallic compounds and increases with temperature. The low values of σ and high Hall coefficient suggest that there must be a deep minimum in $n(E)$ with localized states at the stoichiometric Fermi energy. This will be due to the term $a_{12}(q)$ introduced in §§ 3.2, 4.6, and as explained there will certainly get weaker as the temperature is raised.

Fig. 23

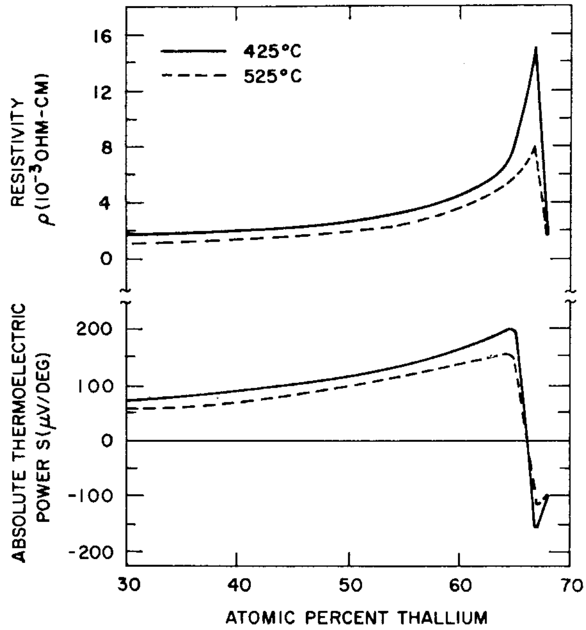


Electrical conductivity σ of some liquid semiconductors (Enderby and Walsh), (*a*) CdSb, (*b*) ZnSb, (*c*) Bi_2Te_3, (*d*) Sb_2Te_3.

Figure 25 shows the temperature-dependence of the resistivity. The rise in ρ at low T for a composition far from the stoichiometric has not been explained.

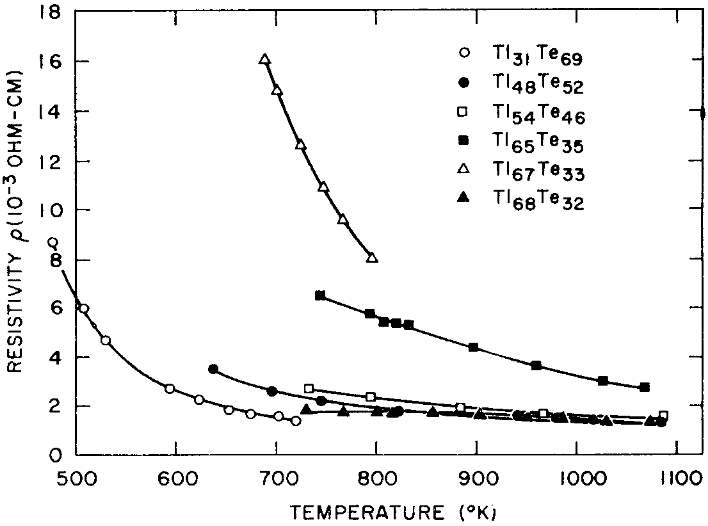
Tellurium-rich compounds are p-like in spite of having more electrons. This suggests that the valence bands are formed by the tellurium atoms, the thallium atoms not contributing states to it. Dr. Allgaier has informed the

Fig. 24



Resistivity and thermopower of molten TlTe (Cutler and Mallon). Curves are uncertain in region of 66% Tl.

Fig. 25



Resistivity–temperature curves for molten TlTe (Cutler and Mallon).

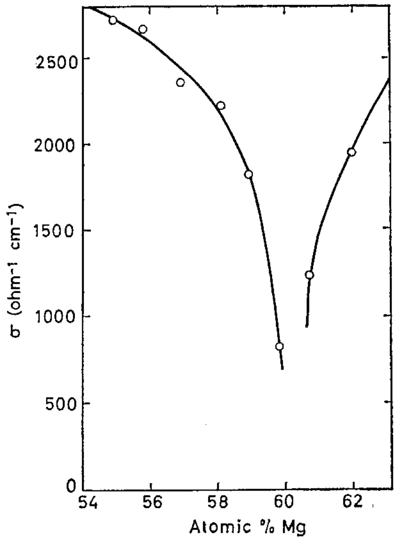
author that Bi–Te behaves in the opposite way, with a minimum at Bi_2Te_3 and excess Te giving n-type behaviour.

Intermetallic compounds show rather similar behaviour. The following table due to Ioffe and Regel (1960) shows some crystalline materials for which there is an energy gap (ΔE):

	Cs_3Sb	Mg_3Sb_2	ZnSb	CdSb	Mg_2Si	Mg_2Ge	Mg_2Sn
ΔE (ev)	1·0	0·7	0·4	0·52	0·77	0·74	0·36

Mg_2Pb has been investigated by Busch and Moldovanova (1962) and—if carefully pumped from gases—shows semiconducting properties with $\Delta E = 0{\cdot}1$ ev.

Fig. 26

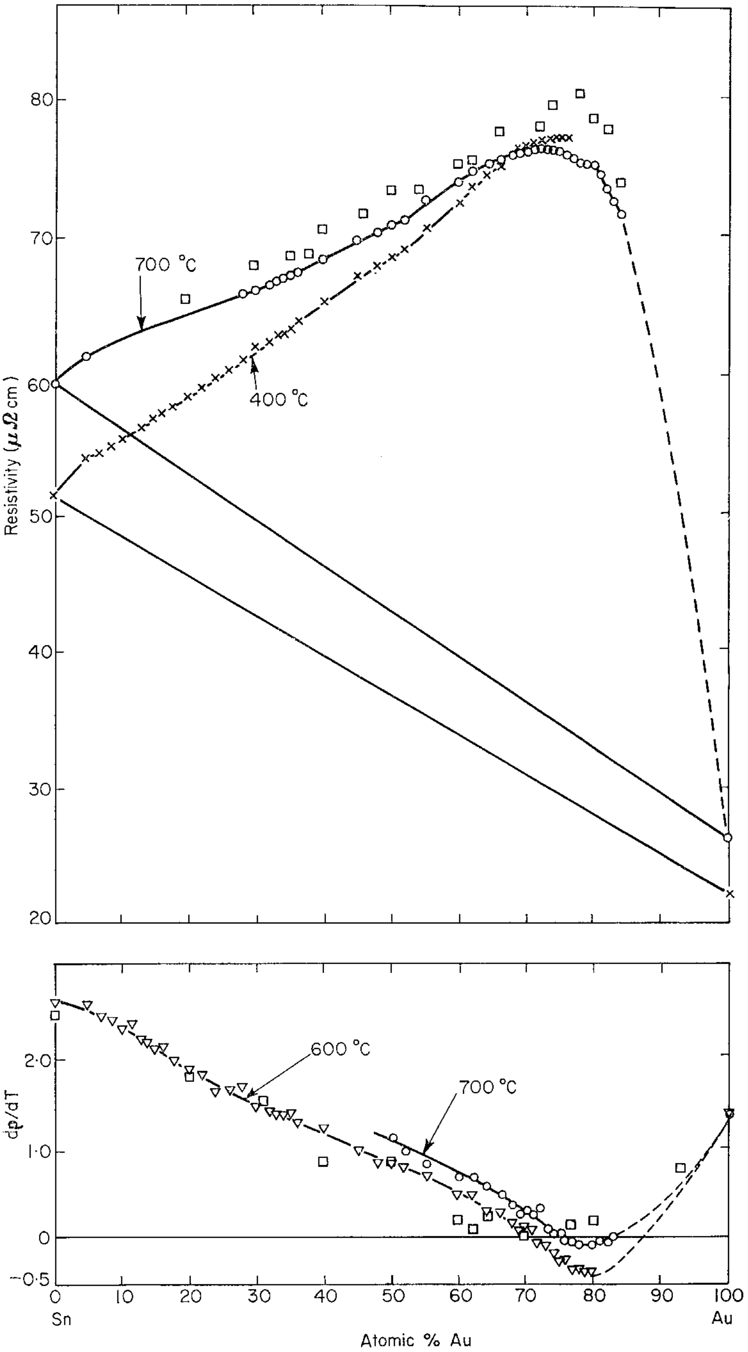


Specific conductivity of liquid Mg–Bi at 900°c (Ilschner and Wagner).

In the liquid state fig. 26 shows the results of Ilschner and Wagner (1958) on Mg–Bi. A similar maximum in the resistance of gold–tin alloys, which have been investigated by Roll and Uhl (1959) and Leach (private communication) (fig. 27). The change in the sign of $d\rho/dT$ near the maximum will be observed. We have no explanation to offer of the position of the minimum.

Dancy (1965) has found similar results for molten CuTe, AgTe and SnTe. The conductivity, of order 1000 $\text{ohm}^{-1}\ \text{cm}^{-1}$, has a minimum at or near the composition Cu_2Te, Ag_2Te and the thermopower changes sign near the same composition. We suggest that these results may be due to a minimum in the density of states rather than to localized states, which are improbable for so high a conductivity (cf. § 6.5). Somewhat similar results for Cu–S, etc., have been obtained by Dancy and Derge (1963), though here the conductivities are lower.

Fig. 27



Resistivity and $d\rho/dT$ for liquid Sn–Au (Leach unpublished).

Busch and Güntherodt (1966) have measured conductivities and Hall coefficients R for liquid Ag–In alloys. A minimum in σ occurs at 35% In, the Hall coefficient at this composition corresponding to two electrons per atom. $d\sigma/dT$ is positive.

6.8. *Mercury*

The behaviour of mercury differs in certain respects from that of other liquid metals and in particular from zinc and cadmium. The abnormal behaviour can be summarized as follows.

(*a*) The melting point (234°K) is very low compared with that of zinc (692°K) and cadmium (593°K).

(*b*) The addition of about 30 at. % of most other metals reduces the resistivity by about 2 (Cusack *et al.* 1964). Some unpublished results by Leach are reproduced by Mott (1966).

(*c*) The thermopower is abnormally high; again on alloying after an initial rise the thermopower drops to normal values (Cusack *et al.* 1964).

(*d*) There is a rapid drop of ρ under pressure. Bradley (1966) has shown that this abnormality disappears on alloying with indium.

The low melting point and cohesive energy have been thought for a long time to be due to the slightly greater s–p separation in the atom (Wigner and Seitz 1955). This is reflected in the slightly more negative pseudopotential than for zinc and cadmium, as shown in fig. 28. Although the difference is slight, it can probably account for the difference in the melting points, in the following way. Details will be published elsewhere, but an outline of the argument is as follows. Heine and Weaire (1966) have given an account of the rhombohedral structure of mercury, based on the curves of fig. 28. They represent the energy of the crystal by:

$$U = U_{\mathrm{E}} - \sum \{v(q_n)\}^2 F(q_n). \qquad (60)$$

Here U_{E} is the electrostatic Ewald–Fuchs term of an array of point charges against a background of 'jellium'. $F(q)$ is $\sum 1/(E_{k+q} - E_k)$ summed over occupied states and q_n are reciprocal lattice points. For cubic mercury the zero q_0 of $v(q)$ would lie very near q_{111}; the band gap there would be small and cubic mercury would have an exceptionally spherical Fermi surface. The rhombohedral structure increases U_{E} and, since $|v(q)|^2$ will increase on the former 111 faces, the second term in (60) is lowered. The change in U_{E} is *ca.* 0·1 ev, and because q_0 lies near $2k_{\mathrm{F}}$, where $F'(q)$ is infinite, the rate of change of the second term is exceptionally large. It just wins over U_{E}, giving a total drop in the energy of 0·01 ev (Weaire, private communication).

Turning now to the melting point, it should of course be possible in principle to calculate the energies of solid and liquid by formulae of type (60) and thus deduce the melting energy and temperature. But, as Harrison (1966) has pointed out, this would need an extremely accurate knowledge of $a(q)$. One can however make an estimate by using the empirical Lindemann melting point formula:

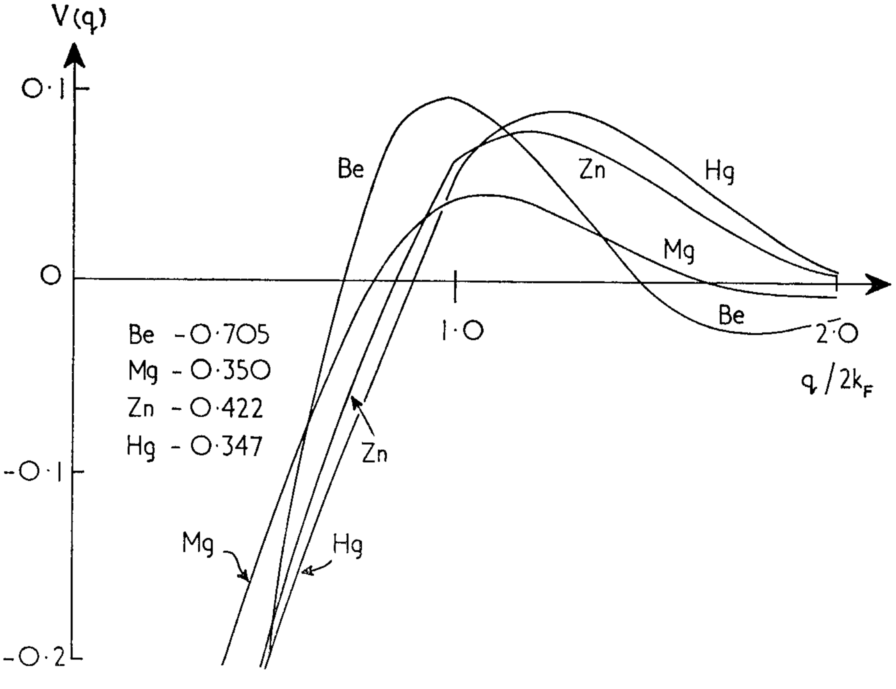
$$M\Theta^2 = \text{const. } T_M/r^2,$$

where r is the interatomic distance and Θ a characteristic temperature. The formula means that T_M is determined by the same stiffness factor as short-wave phonons. If one takes Θ as an Einstein frequency, one can estimate $M(k\Theta/h)^2 = p$, where px is the restoring force when an atom is displaced a distance x. The Ewald term is:

$$k\Theta/\hbar = (4e^2/Ma^3)^{1/2}, \quad 4\pi a^3/3 = \text{atomic volume.}$$

Putting in numbers, for cadmium one obtains $\Theta = 210°\text{K}$ against $172°\text{K}$ observed. It looks as if the second term which should lower Θ is comparatively small, but must be much larger for mercury.

Fig. 28



Pseudopotentials $V(q)$ in Rydbergs of certain metals (Animalu and Heine).

This term (Δp) is easy to calculate. One finds:

$$\Delta p = \sum F(q_n)|v(q_n)|^2 q_n^2 - \Omega \int F(q)|v(q)|^2 q^2\, dq/8\pi^3.$$

The first term should be small for cubic mercury since $v(q_{111}) \sim 0$. The second negative term is very sensitive to the value of q_0. In fact, if we put $v(q) = A(q-q_0)$ and $F(q) = 1$, the integral could be approximated by:

$$A^2 \int q_0(q-q_0)^2 q^4 \, dq = A^2 q_0{}^7/100. \quad . \quad . \quad . \quad . \quad (61)$$

Thus the 10% difference in q_0 between Cd and Hg could double the value of this term, and numerical evaluation shows that the difference in the melting points of these two metals is easily explained thereby.

We turn now to the abnormal electrical properties of mercury. The present author (1966) has attempted to explain them using the following hypotheses.

(1) The density of states of crystalline mercury is abnormally low ($g \sim 0{\cdot}7$) as it is in beryllium, but unlike beryllium $v(q)$ is negative at the zone edges and $|v|$ increases with specific volume. The Knight shift (§ 3) suggests no change on melting.

(2) The cancellation theorem that g does not affect the conductivity breaks down for deviations from unity as large as this.

Since the author's paper, however, the experimental measurements of the de Haas–van Alphen effect (Brandt and Rayne 1966) and the calculations of Keeton and Loucks (1966), using the OPW method, have determined the Fermi surface mercury and shown that the band gaps of Animalu and Heine are approximately correct. Thus $v(q_{111})$ is small and crystalline *cubic* mercury ought therefore to have g very close to unity. Some drop at present uncalculated is to be expected for the rhombohedral structure, and this suggests that the abnormal electrical properties of liquid mercury ought to be due to some distortion of the liquid structure analogous to that for the crystal.

Rivlin *et al.* (1966) have measured $a(q)$ for liquid mercury and have shown that, by comparison with some other metals, the peak in $a(q)$ is displaced slightly to the right and a shoulder appears on the left (fig. 29). According to Heine and Weaire this is due to the same cause as the rhombohedral structure; it lowers the second term in the expression (13) for the energy so as to distort the structure in such a way that $a(q)$ is small near the zero of $v(q)$.

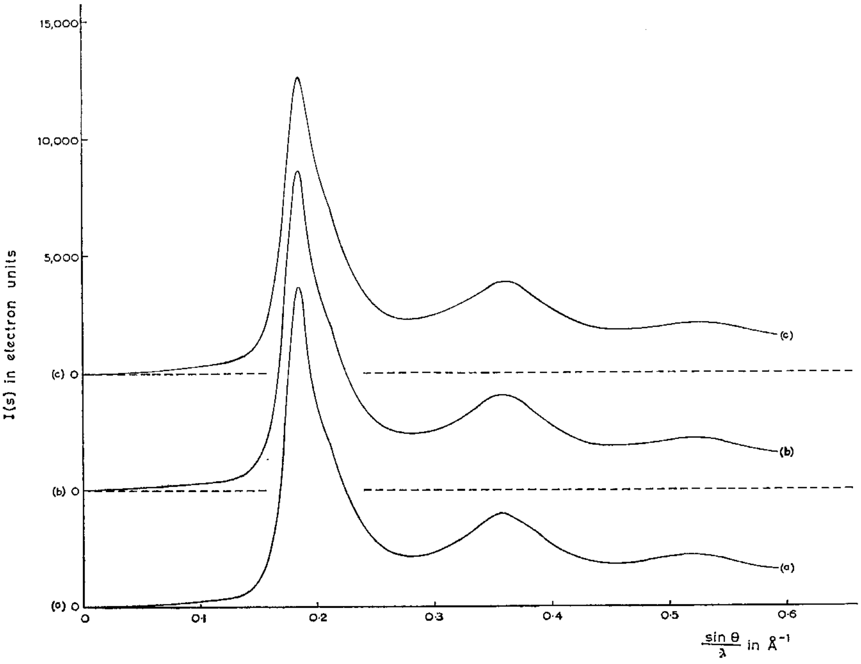
It is therefore tempting to ascribe the abnormal properties of mercury to this abnormal structure, because one would expect that the admixture of any other metal with smaller q_0 would rapidly cause the Ewald term to become greater than the term from $\{v(q)\}^2$, so that the abnormality would disappear. Admittedly no such effect is found in the work of Halder *et al.* (1966) who have measured $a(q)$ for Hg–In; but they do not observe the shoulder at all.

The abnormal properties of mercury, then, may be due to an abnormal shift of the peak in $a(q)$ to the left. This would, according to the analysis already given:

(*a*) Increase the resistivity as calculated by Ziman's theory.

(*b*) Decrease the density of states at E_F. It may be, however, that (*a*) is sufficient to account for the observed effects without the effect of a large abnormality in the density of states; certainly the recent careful observations of $\sigma(\omega)$ by Faber and his colleagues (Smith 1966) do not suggest any effect such as that observed for tellurium (fig. 23).

Fig. 29



Observed values of scattering function for liquid mercury (Rivlin *et al.*), (*a*) −36°c, (*b*) −10°c, (*c*) 27°c. q_0 lies at 0·2 and $2k_F$ at 0·22 Å.

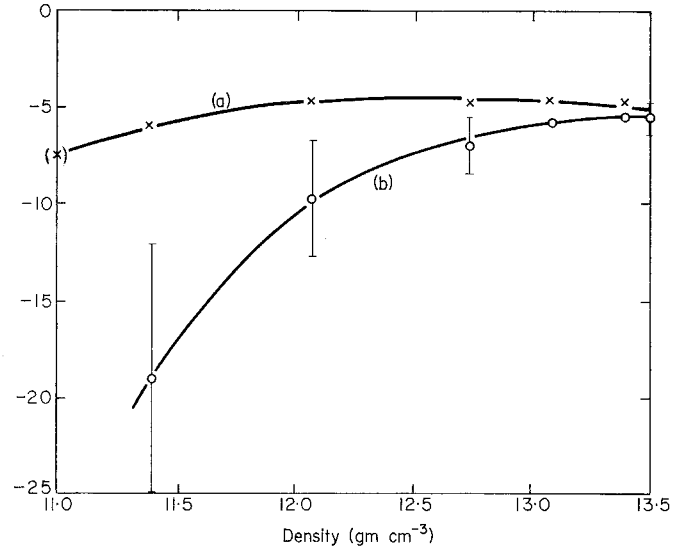
This explanation is compatible with the large increase in σ with pressure; if the lattice is expanded, $2k_F$ moves towards q_0 and the tendency of mercury (either crystal or liquid) to deviate from the close-packed structure will be enhanced (because $F'(2k_F)$ is infinite). We do not however see how to explain the thermopower unless q_0 varies rather rapidly with energy.

6.9. *Liquid Metals at High Temperatures and Pressures*

Early work on the conductivity of mercury at high temperatures is reviewed by Mott (1966). Recent measurements are by Kikoin *et al.* (1965), Franck and Hensel (1966), Hensel and Franck (1966) and Posthill *et al.* (1967). These results, when resistivity is plotted against volume, are of particular interest as showing what happens when a disordered lattice is expanded.

The first thing to remark is that for mercury $d\ln\rho/d\ln T$ is positive and of order 0·2; this is interpreted by Bradley *et al.* (1962) as being due to the widening of the first peak of $a(q)$ and as being normal for divalent metals. Figure 30 shows $(d\ln\rho/dT)_V$ from the results of Posthill *et al.* for varying volume; it will be seen that over this range at any rate this quantity is not large. It seems therefore reasonable to plot ρ against V and suppose that the large changes observed are due to the change in volume, rather than the large change in T. Figure 31 shows the results of Hensel and Franck (1966) plotted in this way.

Fig. 30

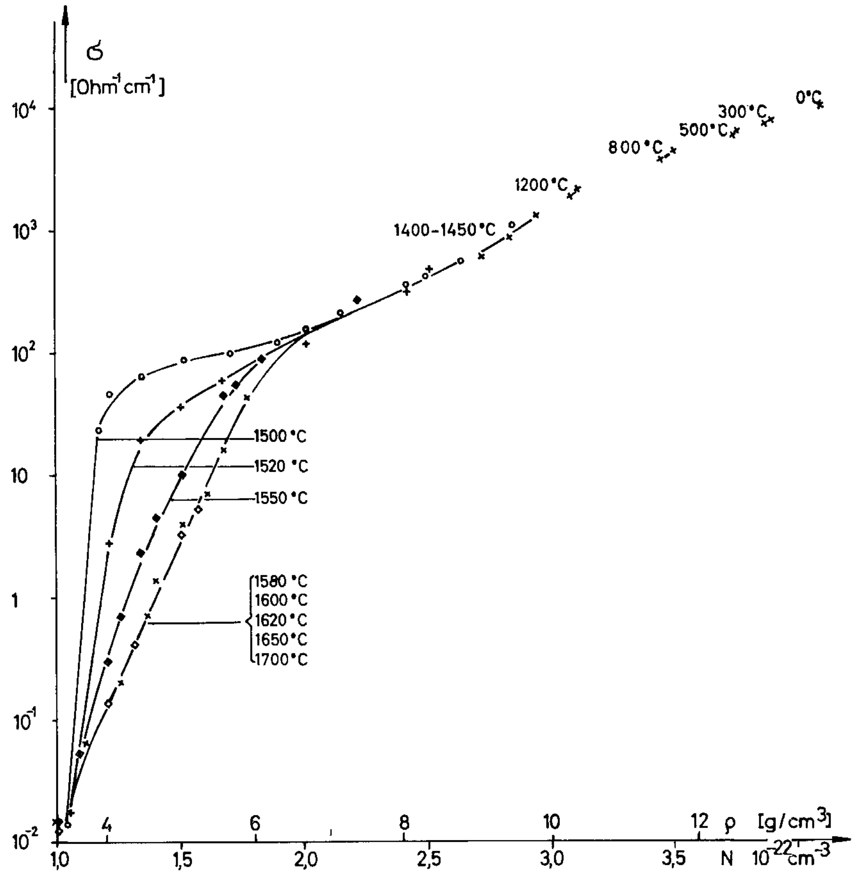


Variation of ρ with T at constant volume for mercury at high temperatures (Posthill *et al.* 1966). (*a*) is $(d\rho/dT)/\rho$, (*b*) is $(d\rho/dT)/\rho_0$. The units are degrees$^{-1} \times 10^4$.

In seeking to interpret these results we must first recognize that as the lattice expands the zero q_0 will move further to the right of the maximum of $a(q)$, so the resistivity as given by Ziman's theory will increase, and the density of states at the Fermi surface will drop. If we are right in thinking that localized states will appear when $g \sim \frac{1}{2}$ and the mean free path is about the interatomic distance (3 Å), the resistivity can drop by a factor about 10–20 before localized states appear. We see that this occurs for a 12% linear expansion. According to our estimates, conductivities between 10^3 and 10^2 ohm^{-1} cm^{-1} should be due to the presence of localized states.

The behaviour round the critical point, where at constant volume the resistivity appears to increase with temperature, is surprising. We suppose that, according to the calculations of the last section, the restoring force when an atom is displaced from a position midway between its neighbours is negative. If so, the liquid may tend to take up a chain structure, which would be broken up as the temperature is raised. This chain structure could perhaps greatly enhance the conductivity.

Fig. 31



Specific conductivity σ for mercury as a function of the density (Franck and Hensel).

The smallest conductivity measured, $2 \times 10^{-2}\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$, if compared with a formula of type:

$$(\nu e^2/akT)\exp(-\Delta W/kT),$$

the constant factor being of order $1000\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$, would imply

$$\exp(-\Delta W/kT) = 2 \times 10^{-5},$$

so a change in T by 100° should only give a change of ρ by 2–3. No change is in fact observed. ΔW should be about 1·1 ev. The interatomic distance is 50% greater than at room temperature. Animalu and Heine's $v(q)$ predicts a band gap on the (111) face of *ca.* 5 ev for cubic mercury expanded to this extent, so it is not surprising if in the liquid there is a real energy gap here of order 2 ev, as this value of ΔW would imply.

§ 7. HEAVILY DOPED SEMICONDUCTORS

7.1. *Introduction*

Under this heading we include:

(*a*) Impurity-band conduction (sometimes called impurity conduction); by this we mean the movement of electrons directly from one impurity centre to another which can only take place if the material is 'compensated' —i.e. contains both n and p-type centres. This kind of conduction always involves thermal activation and is usually but not necessarily a hopping process. It has been referred to already in § 3 and we discuss it in detail in § 7.10.

(*b*) The behaviour of the degenerate electron gas which forms when there is considerable overlap between the centres.

Since in the absence of compensation at any rate the disappearance of conductivity at $T=0$ as the concentration decreases is an example of the metal-insulator transition discussed by the author in a number of papers, we shall discuss this first. Few transitions between a metallic and non-metallic state have been observed as the volume of a *crystalline* solid is changed under pressure. Nearly all the experimental evidence that such a transition exists is obtained from disordered systems, such as doped semiconductors, solutions of metals in ammonia, etc. Observations of transitions under pressure are limited to materials which conduct in d-bands such as V_2O_3 (Austin 1962). This is one reason why a review of this subject is included in this article; the aim is to see what complications are introduced by the non-crystalline structure.

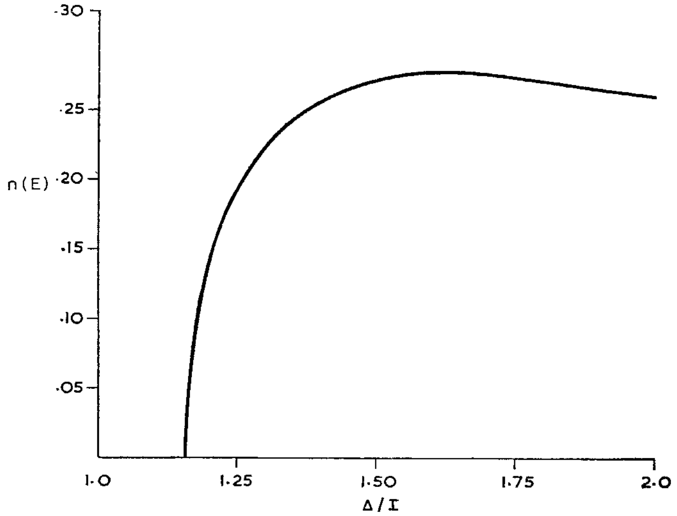
Even in the crystalline state the nature of the transition is not yet entirely clear. We summarize the position as follows:

Verwey and de Boer (1936) and de Boer and Verwey (1937) were the first to emphasize that the band theory of crystalline solids could not be applicable to crystalline materials like NiO, in which the d band is not full but which is nevertheless non-metallic. Mott (1949) discussed the problem further and considered the electrical properties of an array of one-electron atoms; he gave reasons for believing that, as the atomic volume changes at zero temperature, there should be a sharp change of character from a non-metallic phase with no free carriers to a metallic phase with a large density of carriers. These ideas were developed in a number of papers (Mott 1949, 1956, 1961, see also Anderson 1963).

Earlier Wigner (1938) had proposed a similar 'crystallization' of a gas of free electrons with a background of uniform positive charge. Kohn

(1964) has given a formal proof that for sufficiently low densities the crystalline array cannot carry a current. Hubbard (1963, 1964a, b) in a series of papers on correlation in narrow bands has considered the nature of the transition, describing it as a splitting of the d band due to correlation; he does *not* find a discontinuity in the number n of carriers, but this is probably due to his neglect of Coulomb interaction between electrons in neighbouring atoms. What he does find, which goes beyond the author's original formulation, is that the density of states at the Fermi level goes continuously to zero as the transition point is approached (fig. 32).

Fig. 32



Density of states in the neighbourhood of the metal–non-metal transition function of a parameter defining band width divided by interaction (Hubbard 1964).

As regards the Wigner crystallization, the nearest approximation to a uniform positive background would be a doped and compensated semiconductor in which N_A, the concentration of acceptors, was nearly as great as the concentration of donors N_D, and in which both are large. One ought in principle to be able to observe the Wigner crystallization of the N_D–N_A electrons in the conduction band as this quantity is varied. Perhaps the phenomenon nearest to Wigner crystallization that has been observed is the jump in the conductivity of Fe_3O_4 (magnetic) observed by Verwey and Haayman (1941); for a recent review of this substance see Callen (1966). Iron atoms are on equivalent sites such that at low temperatures half are Fe^{2+} and half Fe^{3+}, and the material is an intrinsic semiconductor. At 90°K there is a jump in σ by *ca.* 100 to values of order 100 ohm^{-1} cm^{-1}.

The most direct evidence for the metal-insulator transition comes from the study of the concentration at which metallic conductivity occurs in doped germanium and silicon (Mott 1961, Mott and Twose 1961). This is found to occur for concentrations n such that

$$n^{1/3}a_{\mathrm{H}} \simeq 0{\cdot}2, \qquad (62)$$

where a_{H} is the hydrogenic radius given by:

$$a_{\mathrm{H}} = \hbar^2 \kappa / m_{\mathrm{eff}} e^2. \qquad (63)$$

If the energy is not an isotropic function of κ, this formula needs modifications in ways that have not been investigated†.

In disordered materials, on the metallic side we have to ask what the effect of the drop in the density of states shown in fig. 32 will be. The present author (1966) has made the suggestion that for disordered *monovalent* metals one must use formula (45) for the conductivity, with g dropping with increasing volume as illustrated. This may happen in caesium vapour and other examples are mentioned in this section.

On the insulating side of the transition the effect of disorder is not likely to be great unless an electron is removed from one of the centres (e.g. by compensation). If this is done the states of the hole may be localized and impurity-band conduction by hopping takes place.

In this section we shall first discuss the transition in a crystalline d band, V_2O_3, for which formulae (62), (63) are clearly not valid. We then discuss metal–ammonia solutions and certain other examples of electrons in polar liquids, and then the transition in d bands of doped semiconductors. In much of this work we deal with materials in which there are two dielectric constants κ and κ_0. Under these conditions the value of κ that one ought to use in formula (63) is not clear. Various authors (Simpson 1949, 1967, Pekar and Deigen 1948) have calculated the effective radius of an electron trapped by a positive charge; it should according to Simpson be given by (63) with κ_{eff} given by:

$$\frac{1}{\kappa_{\mathrm{eff}}} = \frac{1}{\kappa} + \frac{5}{16}\left(\frac{1}{\kappa_0} - \frac{1}{\kappa}\right). \qquad (64)$$

The factor 5/16 comes from the assumption of hydrogen-like wave-functions and the use of a variation principle. The only instance known to the author of the use of this equation to describe a metal–non-metal transition is by Sienko (1963) for sodium in ammonia (cf. § 7.3). Cases will be cited below when it is certainly not valid.

Finally in this section we discuss mobility in a degenerate gas and the conductivity by impurity-band hopping.

7.2. *The Metal–Non-metal Transition in d Bands of Stoichiometric Oxides*

An oxide showing d-band conduction on which much work has been done is V_2O_3; this oxide, in common with VO, shows a jump in the conductivity of order 10^5 at a temperature near 200°K. A review has been given by

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† A number of papers estimate the appropriate radius for monovalent atoms, e.g. for the liquid–vapour transition (Meyer *et al.* 1965, Meyer and Young 1965).

Morin (1958, see also Hannay's *Semiconductors*, 1959); the transition temperature drops with pressure and the transition has been observed under pressure (Austin 1962). The theory of the transition has been discussed by Adler and Feinleib (1964), Feinleib and Paul (1965) and by Adler and Brooks (1965), and, as they observe, *given* a d band in which metallic conduction is possible, a transition to an insulating state can occur due to three separate causes:

(1) A splitting of the band due to anti-ferromagnetic ordering, as first proposed by Slater (1951) in general and for this material by Morin (1959).

(2) Correlation, as in Mott's and Hubbard's description of the metal to insulator transition.

(3) A deformation of the lattice.

These authors consider that for V_2O_3 a distortion of the lattice is the most likely hypothesis. They criticize Morin's (1959) hypothesis of antiferromagnetic ordering on the grounds that the existence of magnetic ordering is in doubt, and that even if it occurs, the associated latent heat seems to be much less than observed. To explain the transition they assume that electrons are excited across the gap and that, if electrons are excited, the gap decreases. A temperature T_i at which the gap disappears will then exist. But such a theory, they find, can only explain a change at the transition point of about 10 in the number of carriers. The authors therefore believe that below the transition point small polarons are formed and conduction is by hopping†. Polaron formation is inhibited in the metal because of increased screening by the free electrons.

In this theory the energy gap is 5–8 times kT_i, so the band gap is *ca.* 1/10 ev. The effective mass m_{eff} in the metallic phase is about $50m$ and the mean free path 2 Å.

The small band gap and narrow d band now seem the natural—and indeed the only unforced—explanation of the temperature-dependent transition observed here; the explanation given in Mott (1961) makes a temperature-induced transition a rare accident. But the surprising fact is that metallic conductivity exists at all for so large a value of m_{eff}. The screening distance with $m_{\mathrm{eff}}/m \simeq 50$ will be very small and the inter-ionic distance should be nowhere near the theoretical transition point (62). We believe the explanation may be as follows. In V_2O_3 there are *two* electrons per vanadium atom. If there is metallic conductivity, one has to show that correlation is small enough to allow V^{3+} and V^{+} to be formed as well as V^{2+}. The problem is familiar in the theory of ferromagnetism of the transition metals. Calculations show (Kanamori 1963, Hubbard 1964 a, b) that the electrostatic energy required to change the number of carriers on one d shell is very large (*ca.* 10 ev). Various authors have suggested that this energy is greatly reduced by screening by the s-electrons; the evidence has been

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† One would not expect this at low enough temperatures according to current polaron theory (§ 4.3).

reviewed by the present author (1964, 1965) and by Herring (1966). These arguments emphasize that in the *atomic* state, for instance for nickel, the states $3d^84s^2$, $3d^94s$ and $3d^{10}$ have nearly the same energy. The suggestion that we make here, that the 2p band in oxides can do the same thing, is new; but it seems to be necessary to explain metallic conductivity in V_2O_3 and in similar materials.

7.3. *Solutions of Metals in Ammonia*

There is a very large literature on this subject extending back to the last century. Recent reviews are that by Das (1962), the report of the 'Colloque Weyl' held at Lille in 1963 (Lepoutre and Sienko 1964), and articles by Thompson (1965) and Jortner and Rice (1965). A brief discussion is given here both because metal–ammonia solutions provide one of the best known examples of the metal–non-metal transition and because for dilute solutions the apparent formation of a cavity round a solvated (or rather ammoniated) electron is in marked contrast to the behaviour of electrons in most liquid semiconductors or metals.

For dilute solutions of (say) sodium in ammonia, dissociation is nearly complete. The solvated electron gives an absorption spectrum with a peak in the neighbourhood of 0·8 ev (at $-70\,^{\circ}$c) but with a long tail extending into the visible, which accounts for the blue colour by transmitted light. If the electron is thought to be in a cavity, a radius of 3 Å would account for the volume expansion observed. The absorption band is thought to be an s–p transition for the electrons in one of these centres and the electron spin resonance can be interpreted in these terms (Catterall and Symons 1964).

Theoretical discussions of electrons in cavities have been given by several authors (Jortner *et al.* 1964, O'Reilly 1964). It is not emphasized in all these papers that a cavity can only form if the energy of an electron in the 'conduction band' of ammonia, with random orientation of the dipoles, is *positive*, taking the energy of an electron at rest in free space as zero; the energy of an electron is then lowered by expansion of the liquid. Jortner *et al.* (1965) recognize this in their work on 'bubbles' formed by electrons in liquid helium, expressing it in terms of the 'scattering length' l for the interaction of an electron with the helium atom; the energy of an electron in the conduction band is then $\eta = 2\pi\hbar^2 l/m\Omega$, where Ω is the atomic volume. The authors give evidence to suggest that η is positive for helium and neon, but negative for argon, which agrees with direct calculations of the band structure by Matthiess (1964); bubbles are not formed by electrons in argon (§ 6.2), and the Ramsauer effect is not observed in helium or neon. In helium I or II interesting effects due to zero-point motion and superfluidity occur, which will not be discussed here (Kuper 1961, Clark 1965, Jortner *et al.*, loc. cit.).

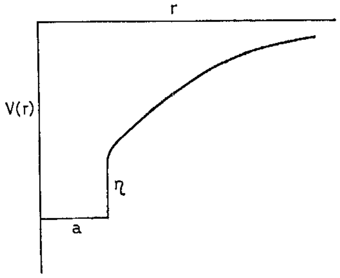
Returning to the cavity in liquid ammonia, a potential well as illustrated in fig. 33 would seem appropriate; outside the cavity of radius a, supposed to contain the electron, the ammonia will be polarized; the field will be

$e^2/\kappa r^2$ and the potential of the electron there is $-e^2(1/\kappa_0 - 1/\kappa)/r$. The energy of the system is made up of:

(1) potential energy of electron $-(\eta + e^2/\kappa_0 a)$,
(2) polarization energy of ammonia $\frac{1}{2}e^2/\kappa_0 a$,
(3) kinetic energy of electron $\hbar^2/2ma^2$,
(4) surface energy of hole $4\pi\gamma a^2$,

where γ is the surface energy. The radius a will be determined by minimizing the sum of these, though a correction to the assumption of a dielectric constant independent of field will be necessary (compare O'Reilly 1964). It will be noted that the magnitude of η does not affect the size of the cavity; but the cavity will only be stable compared with a polaron type of trapping without cavity formation if $\eta > 4\pi\gamma a^2$. Taking the observed value of γ (32 erg/cm^2), and a radius of 4 Å, this would be satisfied if $\eta > 0{\cdot}3$ ev (Jortner, loc. cit., p. 236).

Fig. 33



Potential energy of an electron in a cavity in ammonia or water.

Blandamer *et al.* (1964) point out that the absorption spectra of iodine ions in NH_3 has a maximum at $h\nu = 4{\cdot}0$ ev; the difference 4·0–0·8 ev corresponds closely to the electron affinity of iodine, as we should expect, assuming that the position of the 2p level is determined by the Coulomb part of the field. In water both maxima are shifted by 0·8 ev to higher frequencies; we surmise

$$\eta_{\text{water}} - \eta_{\text{ammonia}} = 0{\cdot}8.$$

The conduction band of water must thus have positive energy of at least 1·1 ev.

Turning now to mobilities, at low concentrations the electron doubtless moves like a heavy ion, carrying its polarized cloud with it. It has however been known for some time that the mobility of a solvated electron is higher than would be given by Stokes' law for the polarized molecules round a cavity of the assumed size (for references see Berns 1965). Probably individual ammonia molecules rotate and move across the cavity (Evers and Longo 1966), but a quantitative description has not been given.

At higher concentrations there is strong evidence that diamagnetic entities are formed; the most direct is that the number of free spins determined by e.s.u. or from the observed paramagnetism drops (Catterall and Symons 1964). Arnold and Patterson (1964 b) discuss the various entities that may form, in particular pairs of electrons trapped in a cavity, like an F′ centre in NaCl. It has been known since the early work of Kraus that the conductivity per dissolved atom drops in this region (by a factor of order 3), so that neutral entities (Na, Na_2) must also be formed. Orgell *et al.* (1964) record a drop in the increase of volume per dissolved atom.

At higher concentrations still there is a rapid increase in conductivity with concentration, which is shown in fig. 34. Arnold and Patterson (1964 a, c) have suggested that this may be a hopping process; if so it should be possible to describe it by a formula of the type:

$$\sigma=(\nu e^2/RkT)\exp(-2R/a)\exp(-\Delta W/kT).$$

This is what Arnold and Patterson do, finding good agreement with experiment if a is 2·54 Å, ν is an electron rather than a phonon frequency and ΔW neglected. We believe there must be an activation energy for a hopping process in a polar solvent. Actually Kraus's values of $d\sigma/dT$ which they quote show a sharp maximum for these concentrations; but the corresponding activation energy is only about 0·15 ev. This must correspond to the *extra* polarization round a doubly charged centre which has to be destroyed before the electron can jump; it is rather surprising that it is as small as this.

We believe that these observations probably should be described with a phonon frequency for ν, and with a Boltzmann factor; this means that, to obtain agreement with experiment, a must be larger than 2·54 Å. The observations could then be explained by an increase in a with concentration c, as c tends towards the value at which the metal–non-metal transition occurs.

The Hall coefficient in this region has been measured by Kyser and Thompson (1965) and rises very rapidly with decreasing concentration. Since the very marked dependence of conductivity on concentration points strongly to some kind of hopping, this is evidence that large Hall coefficients, do occur in this case†.

At higher concentrations a transition to the metallic state occurs; this has been discussed in terms of the author's theory (Mott 1961, Kyser and Thompson, loc. cit., Thompson 1965). But in view of the uncertainty about the model on the non-metallic side of the transition and also the large static dielectric constant, this seems a particularly difficult case about which to make quantitative predictions. However Sienko (1963), in a review of the solubility gap between the metallic and non-metallic phases, comes to the conclusion that formulae (62), (63) describe the transition point well if

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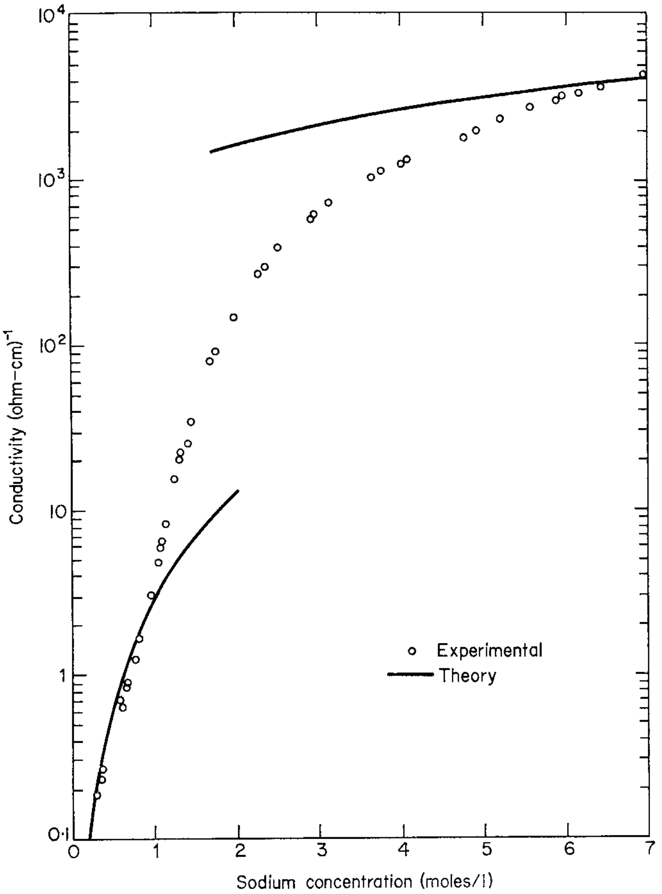
† Dr. Thompson has informed me (March 1967) that there is some doubt about these observations.

formula (64) is used for the dielectric constant. Thompson (private communication) however has found recently that increased temperature *lowers* the concentration at which the transition occurs, though it lowers κ and thus the radius given by (64). The present author supposes that this is because on the insulating side the centres are negatively charged and the polarization energy is lowered by large κ. At low temperatures the solvated electron becomes more stable.

Fig. 34



Electrical conductivity of concentrated sodium liquid ammonia solutions (Arnold and Patterson). The dots are experimental points, the full lines calculated in ways described in the authors' paper.

Of particular interest is the observation (Kyser and Thompson, loc. cit.) that in the metallic region near the transition point the Hall mobility is explicable only in terms of a mean free path less than the molecular size. This is discussed in terms of Hubbard's model (§ 7.1) by Mott (1966). If the conductivity is given by formula (45), and if a small value of g arises through the approach to the transition, then apparent values of L less than the electron wavelength are acceptable.

McDonald and Thompson (1966) have measured the conductivity of the (crystalline) compound $Li(NH_3)_4$, which is metallic, having $\rho \sim 0{\cdot}3\ \mu\Omega$ cm at helium temperature.

7.4. *Metals in Molten Alkali Halides*

This is another system in which the concentration of electrons can be varied. Their properties have been investigated particularly by Bronstein and Bredig (1958, 1961) and Bronstein *et al.* (1962). At the metal-rich end the resistivity increases linearly and rapidly with concentration of halogen; a theory of the scattering based on Ziman's theory has been given by Wilson (1963) and extended by Shimoji and Ichikawa (1966) which successfully accounts for the results, though Wilson's extrapolation to low concentrations of metal with calculated mean free path of order much less than the wavelength can hardly be correct†. The conductivity drops to *ca.* 10^3 ohm/cm, with mean free path of order a, at roughly equal concentration of salt and metal. We should expect localized states to occur for lower concentrations of metal; but of course if they do we should expect some kind of polaron formation, which may be more important in determining the activation energy for hopping than the difference in energy of the states due to disorder.

For low concentrations of metal, in the case for instance of KF at 900°c, the specific conductivity rises rapidly from the value for ionic conduction ($4\ \text{ohm}^{-1}\ \text{cm}^{-1}$) as the concentration rises above 2 or 3 mol. %. A theoretical calculation of the conductivity in this region has been given by Rice (1961). Rice treats the electron as localized on any one of the sodium ions and as hopping onto a neighbouring ion. He is able to estimate mobilities of order $0{\cdot}1\ \text{cm}^2/\text{v}$ sec in agreement with experiment.

7.5. *Tungsten Bronzes*

We turn now to the discussion of the movement of electrons in the d band of a crystalline semiconductor, when the electrons are provided by donors in random positions (in contrast to the case of § 7.2). An example is provided by tungsten bronzes. These materials are non-stoichiometric compounds of the form M_xWO_3, where M is usually an alkali metal and x can range from zero to near unity. Single crystals can be prepared large enough for electrical measurements. They are of interest because a metal–non-metal transition occurs for $x \simeq 0{\cdot}1$, though whether this is a transition of the usual type has been questioned as we shall see.

Crowder and Sienko (1963) have reviewed the properties of WO_3; for the dielectric constants $\kappa_0 = 6{\cdot}25$, $\kappa = 1000$. For the binding energy of an electron in a donor these authors take $I_D = m_{\text{eff}} e^4/2\hbar^2 \kappa_{\text{eff}}^2$ with κ_{eff} given

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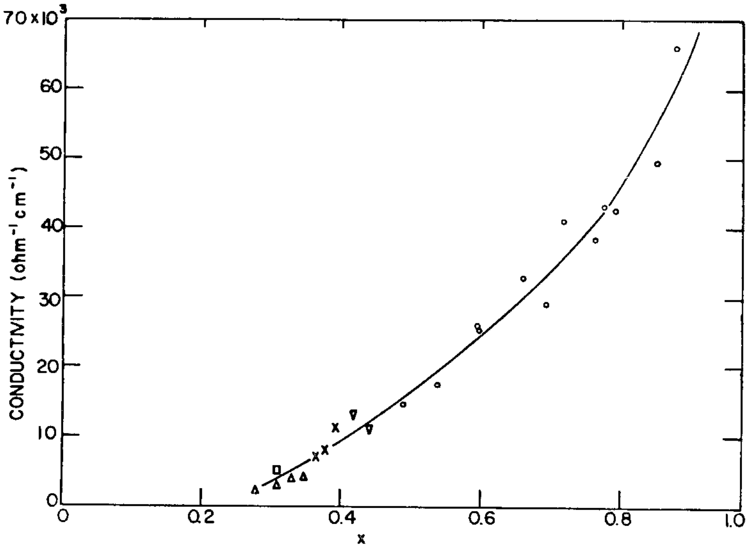
† The considerations of this article suggest that we have a hopping process; the agreement with the calculated values must be fortuitous.

by the formula (64). They state that experiments on lightly-doped WO_3 show that I_D is 0·04 ev, and deduce $m_{\mathrm{eff}}/m = 1{\cdot}2$. Although conduction is in a d band, the effective mass does not seem to be large.

A review of the electrical properties of the bronzes has been given by Shanks *et al.* (1963). The conductivity of a series is shown in fig. 35; we see that the conductivity is high, in the metallic range, for $x > 0{\cdot}24$, and that it depends little on the crystal structure of the bronze or on the particular alkali metal chosen. Figure 36, also from Shanks *et al.*, shows the resistivity of a bronze with small x; the behaviour is that of a normal semiconductor with $\sigma \propto \exp(-\Delta E/kT)$ and $\Delta E = 1/30$ ev. This agrees with the results of Crowder and Sienko (1963) already mentioned.

Fig. 35



Electrical conductivity at 300°K versus x of metallic tungsten bronzes $M_x WO_3$ where M is an alkali metal (Shanks *et al.*).

Both the analysis of the scattering, the high conductivity and measurement of the density of states to be mentioned below suggest that the conductivity is not in a narrow band and m_{eff} is about $1{\cdot}5m$; the value of κ_0 is about 6·2 (Sawada and Danielson 1959) so that hydrogen radius may be between 2–3 Å, and the screening radius similar.

The Hall coefficient has been measured by Ellerbeck *et al.* (1961) for concentrations $x > 0{\cdot}5$; they deduce that one electron per sodium atom contributes to the Hall constant.

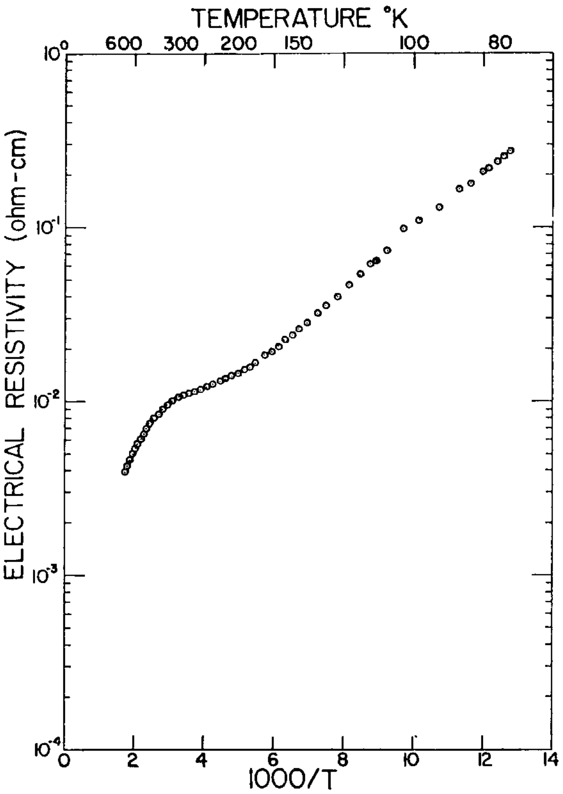
Two theories have been proposed to account for the transition in the tungsten bronzes. Mackintosh (1963) suggests that this is a straightforward metal–non-metal transition; the normal criterion (63) would give $x = 0{\cdot}1$ for the transition, not too far from 0·25 observed. Fuchs (1965), on the other hand, proposes a different theory. The alkali atoms are on definite sites and the atomic radius is small; he proposes:

(*a*) That any cluster in which all sites are occupied is a metal.

(*b*) Any unoccupied site acts like a macroscopic hole, and the effects of boundaries are negligible.

(*c*) No current can pass unless clusters are in contact.

Fig. 36



Resistivity of tetragonal $\mathrm{Li_{0\cdot097}WO_3}$ as a function of T (Shanks *et al.*).

Condition (*c*) leads to the disappearance of electrical conductivity when $x < 0{\cdot}2$ according to calculations of de Gennes *et al.* (1959, see also Domb and Sykes 1961). If this is a true criterion, it is perhaps surprising that electrons cannot ‘tunnel’ between one cluster and another. This may be because each cluster is electrically neutral and it will thus involve an electrostatic activation energy due to image forces when two charged clusters are formed of order $(e^2/\kappa_0 r_0)$, where r_0 is the size of the cluster. A similar model has been used in accounting for the activation energy observed in electrical conduction between metallic microparticles deposited on a non-conducting substrate† (Gorter 1951, Neugebauer and Webb 1962, Neugebauer 1964, Herman and Rhodin 1966).

The evidence that Fuchs puts forward in support of his model is the following:

(1) The electronic specific heat (Vest *et al.* 1958) and Pauli paramagnetism (Greiner *et al.* 1962) have both been measured as a function of x for $x > 0{\cdot}5$. The results show a linear rise with x.

(2) The spin–lattice relaxation time T_1 of the ^{23}Na nucleus has been measured by Fromhold and Narath (1964); the relaxation time is found to be independent of x, suggesting that the local density of states is not changing with x.

The Fuchs model is obviously acceptable (if at all) only when the atomic radius a_{H} is comparable with the interatomic distance. It should be particularly appropriate in narrow band materials.

Finally we record that Bierstedt *et al.* (1966) have recorded superconductivity in certain tungsten bronzes.

7.6. *Titanates and Tantalates*

These materials differ from the tungsten bronzes in that a condensed electron gas can be obtained at low temperature with a small number of donors. The reduced oxide $\mathrm{SrTiO_3}$ has been investigated by Frederikse *et al.* (1964). Here in the stoichiometric oxide the titanium ion has lost all its four outer electrons. A degenerate gas with conductivity tending to a finite value at low temperatures forms on reduction if the concentration of electrons is greater than about $3 \times 10^{18}\,\mathrm{cm}^{-3}$. On the other hand, the effective mass deduced from the conductivity, Hall coefficient and Seebeck coefficient is about $10m$, so in contradistinction to the tungsten bronzes conduction is in a fairly narrow band. The high frequency dielectric constant cannot be high, as the crystal is transparent with forbidden energy gap 3·15 ev (Gandy 1959). On the other hand, the static dielectric constant is very high, 220 at room temperature (Megaw 1957, p. 91, see also Barker 1966, who has measured the temperature and frequency dependence). The low temperature mobility of the heavily-doped specimens is high ($\sim 1000\,\mathrm{cm^2/v\,sec}$) suggesting mean free paths of the order 500 Å and thus a good deal greater than the distance between centres.

In this paper and that by Wemple (1965) unpublished results by Kahn, Frederikse and Becher are quoted in which band calculations have been made and a narrow conduction band based on Ti 3d orbitals found. These are reported briefly at the Paris semiconductor conference (Kahn and Leyendecker 1964).

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† The point made by the earlier of these authors, that current can only flow in an island film if charged islands are formed, and that this requires an activation energy, is questioned by Herman and Rhodin. The present author considers it to be correct; there should be some critical inter-particle distance at which the film ceases to behave as a continuous metallic film, and becomes a sort of semiconductor.

Wemple (1965) and Wemple *et al.* (1966) have measured the behaviour of reduced $KTaO_3$ to see if the substitution of Ta for Ti changes the situations The concentration of carriers lay in the range 3×10^{17} cm^{-3}–10^{19} cm^{-3} and a degenerate electron gas existed over the whole range. The electronic refractive index is 2·3 ; the static dielectric constant is very high, 4500 at zero and *circa* 200 at room temperature. The mobilities μ are higher than for titanates, as the following table shows:

N cm^{-3}	μ (cm^2/v sec) at 4°K	scattering cross section $\times 10^{-16}$ cm^2
$3{\cdot}5 \times 10^{17}$	23 000	850
$2{\cdot}4 \times 10^{18}$	11 000	136
$1{\cdot}3 \times 10^{19}$	3 400	47

The higher mobilities are thought to be consistent with a bigger overlap between the orbitals of the Ta ions.

The existence of degenerate behaviour in these lightly-doped narrow-band semiconductors shows that the high *static* dielectric constant can play an essential role ; the field of the charged ions is effectively neutralised. We find this puzzling. If the electron moves slowly enough to polarize the medium round it, i.e. to form a small polaron—the attraction between the ion and the electron will admittedly be small ($e^2/\kappa r^2$). But at the same time the effective mass will be large. So the condition for the formation of a metallic phase will not be present. The problem needs further investigation. Dr. M. L. Cohen has suggested to the author that the interaction between electrons due to coupling with the phonons may be sufficient to lower the free energy of the metallic state below that of the state in which electrons are trapped†.

The reduced oxide $SrTiO_3$ shows superconductivity (Schooley *et al.* 1964, Schooley *et al.* 1965) over the whole range 10^{18}–10^{21} carriers/cm^3 with transition temperatures in the range 0·1°K to 0·5°K. Theoretical discussions are given by Cohen (1964).

7.7. *d-band Conduction in Ferromagnetic Semiconductors*

Heikes and Chen (1964) have investigated the low temperature conductivity of La doped EuS ; each La atom contributes one electron, and their investigations range from 1–10% La. Their results are shown in fig. 37. They conclude that at low temperatures they are measuring impurity-band conduction, due to compensation from some unknown cause. The same will be true at high temperatures above the Curie point. The large increase in ρ obtained on going through the Curie point they ascribe to a marked

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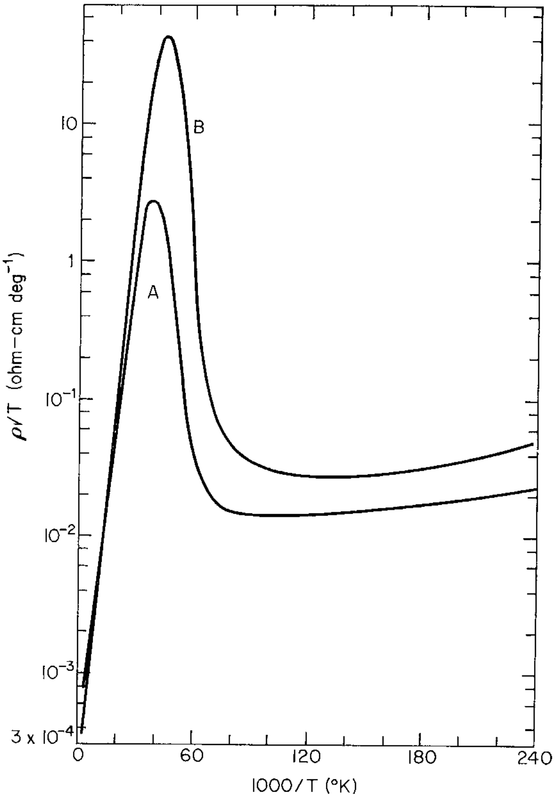
† It is interesting that quite high concentrations of Li (20 atomic per cent, in NiO apparently do *not* give metallic conduction (Ksendzov *et al.* 1963) Kiode 1965, Austin *et al.* (1967). The activation energy drops from *circa* 1·8 ev to about 0·2 ev and flattens off as the concentration increases.

narrowing of the band, with consequent shrinking of the radius of the orbitals of traps, as the magnetization decreases. Such a phenomenon has been predicted by Wolfram and Callaway (1962) who treat the interaction with magnons as narrowing the band, in the same way that interaction with phonons does in polaron theory, but a theory applicable to temperatures above the Curie temperature does not seem to exist.

Fig. 37



Observed values of ρ/T versus $1/T$ for the two La-doped EuS compounds (Heikes and Chen). (A) $La_{0\cdot05}Eu_{0\cdot96}S$ at 26·3°C, (B) $La_{0\cdot1}Eu_{0\cdot9}S$ at 22·5°C.

Similar phenomena have been observed by Methfessel (1965) in a series of crystals of composition $Eu_{1-x}Gd_xSe$. Both Eu and Gd have similar 4f shells but Eu has two other electrons (5d + 6s) while Gd contains five. The conductivity is thus due to x electrons per selenium atom in a 5d band. He reports that recent work by S. von Molnar shows that below the Curie temperature metallic behaviour persists down to $x = 0\cdot01$, and at $x = 0\cdot05$ Hall measurements show 5×10^{19} carriers/cm^3. Recent unpublished measurements by J. D. Axe give $\kappa = 9\cdot52$ and $\kappa_0 = 4\cdot87$. With these comparatively small values we have here also metallic behaviour at a surprisingly low concentration, as in the materials considered in the last section.

The review by Jonker and van Houten (1961) gives many examples of the similar effects of Curie or Néel points on the resistivity of transition metal oxides; see Austin *et al.* (1967).

7.8. *Mobility of Electrons in a Semiconductor where the Electron Gas is Degenerate*

There is a large literature on this subject. To relate it to the theory of resistivity of metals it is necessary to emphasize that it could be treated by Ziman's (1961) theory if one assumes:

(*a*) That the energies at the extremities of the conduction or valence band are of the form $E=\hbar^2k^2/2m_{\text{eff}}$—which is normally not true.

(*b*) That the scattering can be given by the Born approximation. Since the distribution of centres will be almost random, one should take $a(q)=1$ in Ziman's formulae. This is the case for which Edwards (1958) has shown that the Kubo–Greenwood formula leads exactly to the Ziman formulation to the second order in $|V|^2$.

The problem is of course related to that of scattering by ionized impurities in a non-degenerate semiconductor, of which the first theory was that of Conwell and Weisskopf (1950), Rutherford scattering with a cut-off at small angles, and the alternative Brooks–Herring treatment (Brooks 1951; see Debye and Conwell 1954) in which the field due to the ions is analysed into its Fourier components. In the degenerate semiconductor the field of the randomly-distributed ions is screened, and in the Born approximation at any rate a Ziman or Edwards treatment of scattering by individual centres randomly distributed and a Brooks-Herring treatment must be equivalent.

As regards formulae for the scattering by a screened potential in a degenerate gas, that given by Mott (1936) has been extended by Dingle (1955) and Mansfield (1956) and applied by them to degenerate semiconductors. Mansfield finds for the mobility:

$$\mu=3eh^3/16\pi^2e^2m^2f(x),$$

where

$$f(x)=\ln(1+x)-x/(1+x)$$

and

$$x=(\hbar^2\kappa/m_{\text{eff}}e^2)(3n/8\pi)^{1/3}.$$

The substance is only metallic if $x>4$, so

$$f(x)\sim\ln x+0\,(x^{-2}),$$

and we expect μ to vary with n as $1/\ln x$. A slow drop in the mobility is therefore to be expected with increasing n, as:

$$\mu\propto 1/\ln(4x/x_{\text{crit}}).$$

Mansfield plots observed mobility for InSb against concentration; the drop is faster than that calculated. Mott and Twose (1961) took an unscreened Coulomb field extending up to half the inter-centre distance and compared their calculated mobilities with the data of Fritzsche for n-type germanium. Though they find in agreement with experiment that the mean free path is of order of the inter-centre distance (so that there is no question of weak scattering here), the mobility drops faster than predicted by theory. They suggest that the core of the centre may play an important role. If the scattering cross section is independent of concentration n, one would expect

$$\mu = e\tau/m = eL/mv,$$

which is proportional to $n^{-4/3}$.

Gulyaev (1959) and Csavinszky (1962, 1963, 1964) are the only treatments known to the author which go beyond the Born approximation; these authors calculate the s-wave phase shift.

Katz (1965) has given a recent discussion of the subject combined with experimental observations. This work includes investigations of stressed material; the stress separates the three degenerate bands, so that the resistivity due to electrons in a single band can be investigated. For InSb Katz concludes (in agreement with Mansfield, Mott and Twose, *et al.*) that the resistivity of the unstressed material is very considerably (up to 10) above that predicted by any theory, though the discrepancy becomes quite small (*ca.* 2) for the higher concentrations, and is much less marked for the stressed specimens. A very tentative explanation is that the proximity to the concentration at which an insulator transition occurs leads to a lowering of $N(E_F)$ as predicted by Hubbard (1964a, cf. fig. 32), and therefore that a factor g^2 must be introduced into the conductivity formula.

Katz *et al.* (1965) report a T^2 term in the electrical resistance of n-type degenerate germanium which they ascribe to electron–electron scattering type (Baber 1937; for a review see Mott 1964). This depends on the many-valley nature of the conduction band, and disappears when the valleys are separated by stress (Katz 1965).

For compound semiconductors the static polarization of the lattice (shift of the ions) must be taken into account, using for instance the self-consistent quasi-static (Born–Oppenheimer) method of Simpson (1949) (formula 64). For this case we do not know of quantitative calculations, but for large κ we would expect strong screening by polarization. This effect is shown in the observations of Allgaier and Scanlon (1958) and Allgaier and Houston (1962) on mobilities in PbS, PbSe and PbTe. These compounds have very large values of κ. The impurity scattering is very small and the mobilities may be as high as 800 000 cm^2/v sec. Also the mobility drops roughly as $n^{4/3}$, suggesting that the electrostatic field of the centres is negligible and it is only the core that matters. The high mobilities observed by Wemple (1965) in KTaO$_3$ (cf. § 7.6), another substance of very high *static* dielectric constant, have already been mentioned and should have the same explanation.

7.9. *Magnetoresistance in Degenerate Bands*

Many semiconductors in which the electron gas is degenerate show a decrease in the resistance in a weak magnetic field. The effect was first observed by Fritzsche and Lark-Horovitz (1955) and has been investigated by Sasaki (1965) and Sasaki *et al.* (1961). A theoretical explanation was first proposed by Toyozawa (1962 a, b, c) who starts from the argument of Yosida (1957) that localized moments will lead to a negative resistance. If localized moments exist in the gas, the argument is elementary; the scattering cross section by a magnetic impurity will depend on whether it and the conduction electron have parallel or anti-parallel spins. Since the current carried by conduction electrons with the two spin directions are in parallel, the resistivity when the magnetization is M will be of the form:

$$\begin{aligned}\rho &= \text{const.}\quad \left(\frac{1}{1+\alpha M}+\frac{1}{1-\alpha M}\right)^{-1}\\ &= \text{const.}\quad (1-2\alpha^2 M^2\ldots).\end{aligned}$$

It is then argued that in a random distribution of centres there will be certain regions where a localized moment of one or more Bohr magnetons will occur, just as localized moments can occur in d shells of Mn in Cu. To this he ascribes the effect. The normal positive magnetoresistance may take over at strong fields.

The moments are thought to exist at regions of low concentration, just as in Anderson's (1961) theory of localized moments on manganese atoms in copper for example. If so one would expect the effect to disappear at high concentration, and this is found to be the case in heavily doped n-type silicon (Balkanski and Geismar 1966), but not according to Sasaki and de Bruyn Ouboter (1961) in germanium.

At the lowest temperatures these authors have observed anomalies in the resistivity-temperature curve which Sasaki (1965) attributes to the Kondo effect caused by these moments.

7.10. *Impurity-band Conduction*

This term is used in a number of senses. Here we shall use it to mean the motion of an electron from one impurity centre to another, under conditions in which the overlap between the orbitals of neighbouring centres is great enough to allow tunnelling but not great enough for a transition to the metallic state to have occurred. The process can *only* occur if compensation is present. It is usually but not always a hopping process, but always involves an activation energy; we shall develop this theme in this section.

The phenomenon later identified as impurity-band conduction was first observed by Hung (1950) and by Hung and Gleissman (1950, 1954). That this process could only occur when compensation was present was first emphasized by Conwell (1956) and by Mott (1956). The work of

Fritzsche (1958, 1959, 1960) demonstrated experimentally the role of compensation. Mott (1956) was the first to emphasize that the process involved an activation energy. This may occur in various ways, which have been analysed by a number of authors (Kasuya 1958, Kasuya and Koide 1958, Miller and Abrahams 1960, 1961, Mott and Twose 1961, Mycielski 1962 a, b).

At low concentrations, the states will certainly be localized and motion will be by hopping. We may then consider two cases.

(*a*) Very small compensation. Then we have a few vacancies in n-type centres (or electrons in p-type centres) which are bound to the nearest charged minority carrier. The binding energy will be $\Delta E = e^2/\kappa R$, where R is the distance between the two centres so that $R^3 \sim 1/N_{\text{max}}$. The number of free carriers will be proportional to $\exp(-\frac{1}{2}\Delta E/kT)$. The mobility, being due to a hopping process, will also contain an activation energy. This is the case considered by Mott (1956).

(*b*) Moderate compensation. This is the case considered by Miller and Abrahams and probably covers most of the experimental material. All centres must now be treated on the same basis, and the energy difference ΔE between neighbouring centres will depend on the random electric fields due to charged centres of both types. If K is the degree of compensation, then for small K they find $\Delta E = (e^2\kappa_0 R)(1 - 1{\cdot}35\,K^{1/3})$, where $R = (4\pi N_{\text{maj}}/3)^{-1/3}$. For larger values of K, ΔE drops to a flat minimum $(0{\cdot}285\,e^2/\kappa_0 R)$ when $K \sim \frac{1}{2}$.

Miller and Abrahams find for the jump frequency between two states with energy difference ΔE (cf. Pollak and Geballe 1961, p. 1751).

$$1/\tau = 2 \times 10^{12}\,(R/a)^{3/2} \exp(-2R/a) \tanh(\Delta E/kT)$$

where a is the hydrogenic radius of each state. It is clear that, both through the exponential factors in the tanh and through the tunnelling factor $\exp(-2R/a)$, the jump frequency differs greatly from one pair to another. In calculating the d.c. conductivity it is essential to take the easiest path for each carrier, and the d.c. conductivity will be determined essentially by the most difficult step. The d.c. conductivity is the result of an averaging process. Two points of particular interest emerge from the averaging of Miller and Abrahams:

(*a*) the logarithm of the resistivity is proportional not to R but to $R^{3/2}$.

(*b*) the drop in the apparent activation energy ΔE with T, which should occur in a random hopping process, does not appear in their approximation.

The Hall coefficient of impurity conduction in silicon and germanium has been investigated in the hopping region by Amitay and Pollak (1966). No Hall voltage was observed, and this has made necessary some revision of the averaging procedures of Holstein's (1961) theory.

A further consequence of averaging procedures is that the a.c. conductivity should be greater than the d.c. conductivity and *increase* with frequency. This phenomenon has been investigated in detail both experimentally and theoretically by Pollak and other authors (Pollak and Geballe 1961, Sewell 1963, Pollak 1964, 1965).

We turn now to the so-called 'intermediate region', that between the metallic and the region described above. Pollak (1962) has pointed out that observations of D'Altroy and Fan (1956) on germanium at 4·2°K show a conductivity that *drops* with frequency in the microwave region. This suggests that the state of affairs described under (*a*) above can exist *without* the states in the impurity band becoming localized due to disorder. In other words electrons or holes in the impurity band can in this case move by a non-hopping process, with a mean free path of normal type; the observed activation energy for motion is then the energy required to separate the carrier (hole in n-type conductors) from the nearest negatively charged acceptor.

We note that this phenomenon is likely to occur for *small* compensations and for concentrations of impurity just on the insulator side of the transition.

Infra-red measurements have given interesting evidence for the existence of these occupied and unoccupied localized states. Blinowski and Mycielski (1964, 1965) and Blinowski (1966) have given a detailed theoretical discussion of optical absorption by transitions between one localized state and another, when the orbitals overlap, and the phenomenon has been observed by Milward and Neuringer (1965).

7.11. *Glasses and Melts Containing Transition Metal Ions*

Electronic conductivity in these materials is a process very similar to impurity band conduction. It is of course necessary that ions in two states of ionization should be present, for instance V^{4+} and V^{5+}, or Fe^{2+} and Fe^{3+}. In contrast to Fe_3O_4, in glasses the ions may be far enough apart for tunnelling greatly to reduce the conductivity, and in contrast to impurity-band conduction, the activation energy for hopping is likely to be mainly that for polaron formation; the term proportional to $e^2/\kappa R$ will be small because of the comparatively high static dielectric constant κ. We thus expect the conductivity to be of the form:

$$\sigma = \nu c(1-c)\,(e^2/R\,kT)\exp(-2\alpha R)\exp(-W/kT),$$

where ν is a phonon frequency, R is the mean distance between the ions, c, $(1-c)$ are the concentrations of the two valencies, $\alpha=\sqrt{(2mH)}/\hbar$, and H is the energy required to eject a d electron into the valence band. The activation energy W will be made up to two terms; the polarization energy which is half the polaron energy, namely

$$\frac{1}{4}\frac{e^2}{r_0}\left(\frac{1}{\kappa_0}-\frac{1}{\kappa}\right). \qquad (65)$$

and a term of the order $e^2/\kappa R$ which will drop to a minimum when $c=\frac{1}{2}$. r_0 is here the radius of a somewhat arbitrary sphere containing the ion.

As regards the thermoelectric power, the analysis of Heikes and Ure (1961) gives:

$$\text{(cf. § 4.4.)} \quad \alpha=(k/e)\,[\Delta S/k-\ln\{c(1-c)\}]\,; \quad . \quad . \quad . \quad (66)$$

ΔS is the change of configurational entropy when a site is occupied by an electron, and has not been estimated numerically. If ΔS is neglected, the sign will be that of an n-type conductor if c (the concentration of the ion with the mobile electron, e.g. Fe^{2+}) is less than $\frac{1}{2}$. This analysis neglects any spread of energy levels due to the random term $e^2/\kappa R$. This as we have seen in § 4.4 might lead to a larger constant term and an additional term proportional to T.

The numerical value of the quantity H can be roughly estimated from the position of the 'transfer' absorption band of transition metal ions in glasses (Bates 1962), and is of the order 3–4 ev. This would mean that the factor 2α is $18\times 10^8\,\text{cm}^{-1}$; so, if a pair of ions is say 10^{-7} cm apart, $\exp(-2\alpha R)$ is about 10^{-8}.

Turning now to experiment, vanadate glasses have been investigated by a number of authors (Denton *et al.* 1954, Baynton *et al.* 1956, 1957, Munakata 1960, Nester and Klingery 1963, Roe 1965. The paper by Nester and Klingery deals with glasses of nominal composition from 50 to 90% of V_2O_5, the other constituents being BaO and P_2O_5. The thermopower was found to fit formula (66) very well at room temperature, though there was some falling off at low temperatures. Activation energies W in σ for various samples were as in the table, which shows also the high frequency dielectric constant (κ_0):

W (ev)	0·295	0·33	0·392	0·418	0·443
κ_0	4·05	3·72	3·35	3·22	3·15

The correlation between W and κ_0 and the order of magnitude strongly suggest polaron formation according to formula (65). The static dielectric constant was very temperature-dependent and in the range 15 to 50.

There was however some dropping off in the activation energy at high temperatures, suggesting that the activation energy might vary from pair to pair. In glasses the positions of the ions will not of course be random. As regards the tunnel factor, Dr. P. B. Banks (private communication) has plotted $\log_{10}\rho$ against the cube root of the ratio of oxygen to vanadium and obtained as expected a fairly straight line; it is hoped to publish these results in a subsequent paper.

Hansen (1965) has made measurements on iron phosphate glasses with controlled values of c (ratio of Fe^{2+}/Fe) from 0·12 to 0·85. The thermopower is independent of T in the range 150 to 350°C, and satisfies (66) roughly, changing sign as c is increased; but ΔS is not zero. The resistivity at 200°C rises by six orders of magnitude as the concentration of FeO is decreased from 55% to 5%, doubtless due to the tunnel factor, but it is curious that for the 55% composition the author finds agreement with formula (65) *without* introducing a tunnel factor. A plot of resistivity against composition shows a broad minimum round $c \simeq 0{\cdot}5$. At 200°c the minimum is at least ten times deeper than the formula $\{c(1-c)\}^{-1}$ predicts. If this is due to random fields, as in impurity conduction, a short calculation using the formulae of Miller and Abrahams (1960) gives $e^2/\kappa R \sim 0{\cdot}2$ ev, which seems reasonable given static dielectric constants of from 10–20. Thus a significant part, say 20% of the activation energy for hopping may be due to this cause.

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